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Coagulation of colloids by electrolytes as a function of charge and relative concentrations

Elizabeth Folger Tuller
Iowa State College

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COAGULATION OF COLLOIDS BY ELECTROLYTES AS A FUNCTION OF CHARGE AND RELATIVE CONCENTRATIONS

by

Elizabeth Folger Tuller

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Approved:

Signature was redacted for privacy.
In Charge of Major Work

Signature was redacted for privacy.
Head of Major Department

Signature was redacted for privacy.
Dean of Graduate College

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INTRODUCTION

In the study of colloidal systems, particularly of sols, one important phase of investigation has been on the agglomeration and coagulation of the colloidal particle. One of the many controversies in this field has been concerned with the relationship of the purity and concentration of hydrophobic colloids with the coagulation value of an added electrolyte. The coagulation value is usually defined as the concentration of electrolyte (in millimoles per liter) which must be established in the sol in order to bring about coagulation.

Burton and Bishop (1920) have stated a rule attempting to establish a relationship between concentration of a hydrophobe and the coagulation value of electrolytes as follows:

1. The coagulation values of univalent ions increase with decreasing sol concentration.
2. The coagulation values of the bivalent ions remain almost constant regardless of sol concentration.
3. The coagulation values of the trivalent ions vary directly with the sol concentration.

Since the time of the formation of this rule there has been considerable discussion as to the extent of the applicability of these concepts. This controversy has particularly

resolved itself around the application of the Burton-Bishop rule to the colloids known as the hydrous oxides. The first work following the formulation of the Burton-Bishop rule seemed to indicate that the hydrous oxides would be exceptions. Since then it has developed that the purity of the colloid may affect the relation of concentration of colloid and the coagulation value of the electrolyte.

The purpose of the work on which this thesis is based was to resolve this controversy and to show quantitatively the relationship between the purity of the colloid, the concentration of the colloid, and the coagulation value of added electrolytes. The particular colloid chosen for this study was hydrous ferric oxide as it is usually considered as a typical hydrous oxide. Some attention has also been paid to the effect of aging and of the method of preparation of the colloid. The principal object, however, was to attempt to determine the relationship of the purity and concentration of the colloid to the coagulation value of added electrolytes.

HISTORICAL

General Discussion of Coagulation

The stability of the colloidal particle in a hydrophobic system depends almost completely upon the magnitude of the charge on the colloid. The agglomeration of such a system depends on a partial or complete removal of the charge such that coalescence may take place. When agglomeration takes place to an extent that sedimentation will occur at a rate dependent on the size of the particle, the phenomenon is called coagulation.

The general distribution of the charge in a colloidal micelle is believed to be that indicated by the electrical double layer theory. Briefly, this theory as finally developed indicates that there are two layers of charges. There is a fixed, rather condensed layer of charge attached to the particle itself. The second layer is a more diffuse movable layer--an ionic atmosphere surrounding the charged particle. The movable layer controls the sign and quantity of charge of the particular colloid. The gradient in this layer is usually known as the zeta potential or the electrokinetic potential. In coagulation most authorities agree that there is a partial or complete neutralization of the movable layer; i.e., it is said that the zeta potential is partially or

completely reduced. There is also another term used in this connection--critical potential. The critical potential is the name applied to the zeta potential in the critical zone, which is that potential zone in which coagulation takes place. The size of the zone varies with the properties of the colloid and with the concentration and nature of the added electrolyte.

Mechanism of Coagulation

The mechanism of coagulation has been the subject of much investigation. At the present time there are about four popular theories.

The solubility theory, first propounded by Declaux (1899), is probably the oldest of the four. As it has been expanded and modified by Pauli and Matula (1917) and finally by Pauli and Valko (1926), coagulation is believed to consist essentially of a chemical change involving the precipitation of a difficultly soluble electrolyte. The supporters of the theory believe that colloidal particles are highly complex ions resulting from the ionization of complex electrolytes allied to Werner-type compounds. The reaction of these complex colloidal electrolytes with the added electrolyte, to form difficultly soluble compounds, causes the phenomenon known as coagulation. There is no attempt to give an exact chemical formula for the colloid or complex electrolyte, nor for the

difficultly soluble compound formed. To the contrary, all attempts to find such formulas have ended in failure. This, however, does not necessarily invalidate the theory.

A rather interesting but less well known theory of coagulation is that proposed by Hauser and Hirshon (1939). Their theory might well be called an orientation and condensation theory. Coagulation is believed to take place in two steps. Orientation, the first step, takes place when the forces acting in the system are sufficient to cause the particles to arrange themselves in minimum energy positions with respect to each other and to the surrounding ions. In the second step, condensation occurs when the system as a whole contracts; this step is controlled by electrical forces. The rapidity and completeness of orientation and condensation depend on adsorption characteristics of the colloidal particles and of the ions as well as the sign of the charge of the coagulating ion. The authors believe that their theory explains gelation, purity, and concentration effects in coagulation studies. Their explanation of the Burton-Bishop rule depends upon the relative adsorption of the ions of the added electrolyte. Upon the addition of univalent ions to a concentrated sol condensation takes place around one ion while the other oppositely charged ion compresses the double layer. In the dilute sol coagulation must take place primarily by the reduction of charge due to the ion of the opposite sign; hence a larger concentration of electrolyte is necessary. Likewise,

according to these authors, coagulation by polyvalent ions occurs primarily by neutralization of charge through adsorption of the ions. The extent of the adsorption is determined by the concentration of the ions in the solution. With concentrated sols considerable entrainment occurs, necessitating more electrolyte than in the dilute sols in which little or no entrainment occurs.

The two theories of coagulation most prominent today are the adsorption theory, first expounded by Freundlich (1909), and the activity coefficient theory proposed by Ostwald (1935).

The adsorption theory has been developed and examined for many cases. Weiser (1931), besides reviewing the adsorption theory in general, has considered the application of the theory to the hydrous ferric oxide sol. The assumption is made that particles of hydrophobes owe their charge to the preferential adsorption of ions from the intermicellar solution. Addition of an electrolyte causes coagulation as a result of the preferential adsorption of the ions of charge opposite to that on the colloidal particle. This preferential adsorption lowers the zeta potential to some critical value, and coagulation takes place. Thus Weiser (1931) defines the coagulation value of an electrolyte as that concentration leading to sufficient adsorption to neutralize the charge on the colloid below a critical value.

According to Kruyt (1930) the effect of the concentration of the sol on the coagulation value is dependent upon

two factors. One factor is that the dilution of the colloid draws the particles farther apart and decreases the probability of collision. The second factor has to do with the quantity of the ion adsorbed at the coagulation value. In the case of the univalent ion this amount is very small, but in the case of the trivalent ion nearly all is adsorbed. In the latter case a definite interdependence must exist between the coagulation value and concentration.

For the univalent ions, the second mentioned effect is small and therefore the first predominates; thus the concentration of electrolyte needed increases with dilution of the sol. For trivalent ions, the second effect predominates and the electrolyte needed decreases with dilution of the colloid. The divalent ions occupy an intermediate position in which the two factors balance and the amount of electrolyte needed for coagulation is almost independent of the concentration of the colloid.

A theory which has been developed admittedly only for coagulation with neutral salts is the activity coefficient theory. Ostwald (1935) considers the hydrophobe sol as a mixed crystal with the large micelles considered to be a highly dispersed ionic lattice. The coagulating force is supposed to be similar to interionic attraction forces. Therefore coagulation will take place at the same activity coefficient value for different electrolytes.

Any adequate theory of coagulation must be able to

explain all the phases of coagulation effects noted. Particularly the theory must be able to explain the role of the secondary ion, i.e., the ion of the same charge as the colloid. To date, none of the above theories completely explains coagulation of hydrophobic sols.

Kinetics of Coagulation

There are two general types of coagulation: (1) that involving nearly complete removal of electric charge in which the zeta potential equals zero; and (2) the partial neutralization of the charge in which the zeta potential is not equal to zero but a critical potential has been reached. The first type is usually considered as being rapid coagulation, and the second is known as slow coagulation. In general, a relatively high concentration of electrolyte usually results in rapid coagulation. The difference between rapid and slow coagulation is indicated not only by a difference in the neutralization of charge but a difference in the physical behavior of the colloid. For example, the size of the particles in the coagulum and the rate of sedimentation vary with the rate of coagulation. Rapid coagulation usually produces small compact massive particles which settle rapidly. Slow coagulation tends to produce large loose aggregates that settle slowly.

The first attempt to find a quantitative expression to indicate the rate of coagulation seems to have been made by von Smoluchowski (1916). He developed an equation to express

the laws of probability governing the collision and adhesion of the colloidal particles. The initial attempts were concerned only with sols containing only primary particles, i.e., monodisperse sols.

For monodisperse sols von Smoluchowski's equation is

$$n_1 = \frac{n_o}{(1 - \rho t)^2}$$

where n_o is the number of primary particles in unit volume at zero time, n_1 is the number of doublets at time t, and ρ is a constant which is equal to $4\pi DRn_o$. In this latter expression D is the diffusion coefficient and R is the radius of action.

Since this equation takes into account only the primary particles agglomerating into doublets, the summation of equations taking into account the agglomeration of several primary units results in the relation

$$n_t = \frac{n_o}{1 - \beta t}$$

where n_t is the total number of particles at time t.

Numerous investigations have supported the equations of von Smoluchowski for rapid coagulation of monodisperse sols. However, the equations do not satisfy experimental results for slow coagulation or for sols containing particles of various sizes, i.e., polydisperse sols. Weigner and Muller (1926) were the first to attempt to give an equation for the rapid coagulation of polydisperse sols. Von Smoluchowski (1917) himself modified his equations in an attempt to meet the

conditions found in slow coagulation. However, there has been no adequate confirmation of his equation but merely a production of as many other equations as investigators in this field. Von Smoluchowski's theory does seem to hold with very dilute colloids studied under the ultramicroscope but is not otherwise adequate.

Recently Yodava and Chatterji (1944) have pointed out that examination of the various equations proposed to evaluate the rate of coagulation shows that in rapid coagulation the time taken to reach a given stage of agglomeration is the same when various electrolytes are added, provided all conditions are the same other than the concentration of the electrolytes.

Two more or less qualitative methods of indicating the rate of coagulation have been proposed. Mukherjee and Papaconstantinou (1920) suggested that the reciprocal of the time necessary to reach the limiting light absorption values measures the rate of coagulation. This would be applicable to photometric methods of following coagulation. Fodor and Riwlin (1928) have indicated that the tangent to the curve of opacity against time cuts the x- axis in an angle indicative of the rate of coagulation.

In the course of the many studies on rate of coagulation, the phenomenon of autocatalytic action has been noted. However, there is considerable controversy over the presence of this autocatalytic action. Autocatalysis is shown when the course of coagulation is plotted against time. For example,

if viscosity change is plotted against time, the function is an S-curve characteristic of autocatalysis.

The presence or absence of the S-curve seems to depend in part upon the purity of the sol. In fact, Patel and Desai (1930) have indicated that there are four items which affect the S-curve and hence the autocatalytic nature of the coagulation. These four factors are: the concentration of the added electrolyte, the purity of the colloid, the charge on the colloid, and the concentration of the colloid. According to these investigators, dialyzed sols show less and less tendency for autocatalysis until there is a final disappearance of the S-curves. The curves also become steeper as the concentration of the electrolyte is increased and the charge on the colloid is decreased by dialysis, which removes the stabilizing ion. As the colloid is diluted, the S-shape decreases for the same concentration of electrolyte.

Hildebrand and Sorum (1934) confirmed some of these results by showing that highly purified sols do not show autocatalysis. Ghosh (1934) has pointed out also that the S-curve is more definite with lyophilic colloids than with strongly lyophobic colloids. Korchor and Patel (1934) indicated that the more strongly the stabilizing ion is adsorbed, the greater the autocatalytic nature of the coagulation; i.e., the S-curve will be more prominent.

Concentration of the Colloid and Coagulation

In the search for a quantitative relation between the valence of the coagulating ion and the coagulating power of that ion, it developed that the concentration of the colloid played a definite part in the coagulation phenomenon. Kruyt and van der Speck (1919) were the first to recognize this phenomenon. However, the rule indicating the relationship of concentration of the colloid, the valence of the coagulating ion and the coagulating power of that ion has become known as the Burton-Bishop (1920) rule. As previously mentioned, this rule indicates that the coagulation values of monovalent ions vary inversely with the concentration of the colloid, of bivalent ions are independent, and of polyvalent ions vary directly with the concentration of the colloid. The majority of this work, however, was done with negative hydrophobes; relatively little attention has been paid to the strongly hydrophobic positive sols.

Weiser and Nicholas (1921) attempted to confirm the Burton-Bishop rule using the hydrous oxides. Their experiments led them to claim that this rule would not hold for the positive colloids of the hydrous oxide type, and the conclusion appeared to be confirmed by Sen and Dhar (1922). However, using a specially purified hydrous ferric oxide sol, Judd and Sorum (1930) showed that the Burton-Bishop rule held. They laid this correlation of concentration of the colloid and coagulation value of the electrolyte to the high purity of the

colloid. In an attempt to show that the purity of the colloid was the controlling factor in the behavior of the sol, Sorum in his original work and in a later investigation conducted by Fisher and Sorum (1940) added a small quantity of ferric chloride to the pure sol. The addition of the ferric chloride caused a reversal of the behavior of the sol; thus it no longer followed the Burton-Bishop rule. Although Dhar (1930) challenged the work of Sorum on the basis of that of Sen, Ganguly and Dhar (1924), Ghosh and Dhar (1925), and others, Sorum (1931) pointed out that the sols used were not of sufficient purity.

Later, Kaufmann (1940) and Tuller and Eblin (1944) confirmed the work of Sorum. Moreover, the latter authors found that sols containing more chloride than those used by Sorum may follow the Burton-Bishop rule. Weiser and Milligan (1940) have pointed out that the Sorum effect is to be expected; the purer sol is more unstable to electrolytes and upon dilution becomes relatively more stable. Hence the sol formed by dilution of an unstable preparation would be more stable than the sol formed by dilution of an impure highly stable preparation. They thereby restated the Burton-Bishop rule as follows:

> For a given sol, the proportionate increase in stability toward precipitating electrolytes on dilution is in general greater for electrolytes with univalent precipitating ions than for electrolytes with multivalent precipitating ions, and is greater the higher the purity of the original sol.[1]

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[1] Weiser, N. B., and Milligan, W. O., J. Am. Chem. Soc., 62, 1929 (1940).

Measurement of Coagulation

Coagulation values have often been determined as the concentration of electrolyte (in millimoles per liter of final solution) needed to produce coagulation in a given length of time. Coagulation was determined by observing the settling of the coagulated colloid such that a few millimeters of clear supernatant liquid were visible. This, however, was only an approximate method.

The most basic method of determining complete coagulation is the direct observation of the phenomenon with the ultramicroscope. Since, however, this is a long tedious process usable only with dilute colloids and is not easily adaptable to following the rate of coagulation, a number of other indirect methods have been employed.

One of the oldest methods, now used infrequently, is based on the titration of the supernatant liquid. Paine (1913) first used this method in studying the coagulation of a copper sol. At about the same time Freundlich and his co-workers (1913) utilized the measurement of viscosity as a method of following coagulation. A number of investigators have continued to use this procedure. Rabinovich and Korgin (1929) introduced the use of the glass electrode in following coagulation through pH changes.

Aside from the above-mentioned methods of measurement, the most commonly used determinations are those involving

some type of optical measurement. These optical measurements include turbidimetric, nephelometric, spectrophotometric, spectroscopic, colorimetric, photometric, and light polarization methods.

Turbidimetric methods were first used by Lattermoser (1914) in coagulation measurements on sodium tungstate sols. Since that time turbidimetric and nephelometric methods have been employed extensively by various investigators. Those methods have been improved by the use of thermocouples and photoelectric cells so that the accuracy does not depend upon visual judgment.

Colorimetric methods have not had as wide use since they depend upon a change of color of the colloid. However, they were used first by Hatschek (1921) in following the coagulation of a gold sol.

Likewise, spectroscopic methods have not been employed to any great degree although the first mention of them was by Krishnamurti (1928).

The work of Jogarao (1937) on the measurement of polarized light both in the horizontal and vertical direction as a means of following the coagulation of a colloid formed the basis for much other work utilizing these principles. However, most of the work has been with respect to the properties of the colloids and the depolarization of light rather than following the coagulation phenomenon.

Mukherjee et al. (1920) were the first to use

spectrophotometric and photometric methods. Since that time various types of these instruments have been employed. The spectrophotometric methods have depended primarily on the use of a Nicol prism and the measurement of the angle of rotation of a beam of light sent through a dispersion prism. The other photometric methods have used glass absorbents and have depended in their measurements upon a change in aperture, a change in the distance of the source of light, or on the sensitivity of a photocell to changes in light intensity.

The most recent work has been done by two principal groups. Prasad and his co-workers (1940) employed photometric apparatus using a photocell and visible light. The second group, working in Wannow's laboratories, have been using modifications of an instrument built by Wannow and Hoffmann (1937), utilizing ultra-red light. However, Kaufmann (1940) has reported on the use of another method to supplement the methods of Wannow and Hoffmann. According to Kaufmann, the methods are not too satisfactory with dilute hydrous oxide sols; therefore he centrifuges the coagulating material after a definite time interval following addition of the electrolyte and compares the Tyndall cones of the supernatant liquids. He defined complete coagulation as the point at which the Tyndall cone disappeared.

For the most part, coagulation values are determined by the concentration of electrolyte necessary to produce a certain effect in a given time determined by measurements as

described above. That is, the limiting values of degrees of turbidity, angles of rotation, intensities of light, and other criteria are indicative of changes in the colloid. These methods are good only for comparison purposes but not for absolute data. In other words, curves may be drawn indicating trends.

Wannow (1936) described a method of determining coagulation values in which he first plotted the relative transmittancies against the time for various concentrations of electrolytes. He then plotted the relative transmittancies for a specified time (such as five minutes) against the activities of the coagulating (dominating) ion. This last curve is S-shaped with a sharp inflection point. The concentration at that inflection point is taken to be the coagulating value. He points out that this method also is good only for comparison purposes for the same electrolyte on colloids in various conditions but not for absolute values; the method developed used a Zeiss nephelometer. However, Wannow (1937) later stated that his method gave absolute values when used in connection with data taken with his ultra-red photometric apparatus. He based his belief in the use of such a method upon the fact that the curve obtained by plotting the number of particles in a given time against the activity coefficient of the coagulating ion showed about the same course, particularly the same inflection, as did the corresponding curve of light transmission against activity coefficient. In other

words, transmission as well as the number of particles decreases greatly in the sphere of flocculation. Hoffman and Wannow (1938) reported on the experimental work showing the above correlation which had been used in their previous studies on coagulation.

Troelstra and Kruyt (1943) took exception to the above method of Wannow as a method of determining the coagulation point. As they point out, the inflection point will vary depending upon the time picked. That is, the inflection point for the curve based on transmission at two minutes will not be the same as that taken at five minutes, and so forth They, therefore, do not believe that it is characteristic of the coagulation capacity of the electrolyte used. In fact, they very much question whether it is of as much importance as the coagulation point found in a more primitive way.

The extinction of light by an agglomerating colloid will depend upon two factors according to Troelstra and Kruyt (1943). Those two factors are the velocity of agglomeration and the structure of the flocculate. According to these investigators a loose aggregate scatters less light than a massive sphere of the same size. They also question the standard method of investigating coagulation by determining sedimentation in a given length of time because it indicates not only coagulation but a length of time for sedimentation itself. That is, differences in the rates of coagulation will tend to cause the formation of different kinds of

aggregates which in turn settle at different rates. The slower the coagulation, the longer the time of sedimentation. Therefore, from the point of view of kinetics it would be better to choose a certain degree of particle number in a definite time as the criterion for investigation of agglomeration. It is more important to know where deformation of the double layer occurs even though it might not lead to complete coagulation. But, at least, a method should be chosen, such as the color change of a gold sol, which indicates a certain aggregation degree independent of the occurrence of sedimentation.

Hydrous Ferric Oxide Sols

It is well known that dialysis and aging of colloids may affect many of the properties including particle size, viscosity, conductivity, electrophoretic mobility, charge, stability, and so forth.

For this particular study it is of particular interest to know how the particle size, charge, and stability vary with dialysis and aging. It is also important to know what changes occur in the colloid upon dilution.

Nichols, Kraemer and Bailey (1932a) in two papers have discussed at length the change of particle size with the time of hydrolysis of ferric chloride and the effect of aging and dialysis. Their method of hydrolysis was to reflux a dilute

solution of ferric chloride for a given length of time. Their work indicates that for colloids prepared with ferric chloride, up to 0.037 M, the sols are reasonably reproducible and may be diluted with water or very dilute hydrochloric acid with little or no appreciable effect on the particle size. Their studies also show that the hydrolytic process is rapid and that digestion favors secondary processes of dehydration and growth of crystal size. They also point out that the size of the primary particles does not vary much with the concentration of ferric chloride used, but that the rate of growth is more rapid with higher concentrations of the salt.

Upon dialysis of a day-old colloid Nichols et al. (1932b) found that, in spite of some evaporation and osmotic dilution in 24 hours of dialysis at a purity of 21.6, a negligible shift of 3.8-4.4 mm. in mean radius took place; the value 21.6 refers to the ratio of equivalents of iron to equivalents of chloride. At the end of the dialysis reported, there was a small flocculated sediment. The authors concluded that the removal of acid and salt did not greatly affect the particle size. They pointed out that the slight shift might be due to the presence of fresh sol produced through further hydrolysis of ferric chloride before the latter was removed by dialysis. Apparently they did not consider that complete hydrolysis of the salt had been reached. Since there was a definite increase in particle size when the dialyzed sol stood, it was concluded that the stability was

reduced by dialysis. This, of course, checks with all the work that has been done in determining stability by coagulation studies.

They also found that upon aging an undialyzed sol, there was repeptization of the colloid reducing the colloidal iron content and increasing the ionic iron. There was also an increase in the particle size. The extent of the shift was greatest for those sols made from the more concentrated ferric chloride solutions. The behavior of the aged and freshly dialyzed sols was discussed. The purities of both types of sol reached the same point, and the colloidal iron content of the aged sol was increased presumably by hydrolysis of the ferric chloride.

Nichols, Kraemer and Bailey (1932b) discussed two other interesting facts. First, the aging of the sol caused the absorption of visible light to decrease to about half its original value. Dialysis of the fresh sol brought about a large increase in light absorption. The former effect is probably due to the repeptization action while the latter is due to a change in the composition of the sol. Secondly, the investigators pointed out that the age of the stock solution of ferric chloride used made a slight difference in the particle size of the colloid. However, the data indicated the shift to be of the same order as that caused by dialysis provided the stock solution is at least two weeks old. The

least shift appears to take place if the stock solution is between two weeks and three months old.

Ellison and Hazel (1935) investigated the effect of concentration and age of the ferric chloride solution on the colloidal properties of hydrous ferric oxide. Unfortunately the most concentrated solution they used was M/10 and much of their investigation was with M/100 and M/1000 concentrations. They pointed out that, as the ferric chloride solutions age, there is an increase in the number of particles formed in the colloid prepared from the salt solution. They also pointed out that after the first step there is a linear relation between the pH and the number of particles in the colloid (original sol).

Ayres and Sorum (1930) maintained that with temperatures of hydrolysis of 100-145° C neither the temperature nor the concentration of the ferric chloride used affected the particle size to any great extent. Particle sizes ranged from 52 to 76 millimicrons, with an average of 60. Examination of the data shows that 80 per cent of the particle size range is from 54 to 66 millimicrons. There is no apparent order to the way the particle size varies with temperature of hydrolysis. It is also true that, according to the figures given, the ferric oxide concentration varied considerably with no particular correlation with the size of the particle. There also seemed to be no correlation of temperature, ferric oxide content, and the original molarity of the ferric chloride

solution used. Surprisingly enough, the authors reported first that there was little or no difference in the particle size at lower or higher temperatures, while their next statement was to the effect that at the higher temperatures there was some sediment which was centrifuged off before determining the particle size. Sols prepared at lower temperatures, however, were clear and stable.

The pH of the hydrous ferric oxide colloid changes slightly on standing. According to Fuks and Rabinerson (1936), this pH change is due to the slow hydrolysis of the ferric salt. Equilibrium in their experiments was reached in three to six days.

Apparently, dilution has little or no effect on particle size since Jablezynski and Sowaniak (1936) as well as Nichols et al. (1932a) have found no difference even up to 120 hours after dilution. However, according to Fuks and Komsalova (1935) the dilution of concentrated sols destroys the secondary structure and displaces equilibrium. This effect is greater with aged sols. Kruyt and Klampé (1943) have questioned work on the relationship of sol concentration and electrolyte resistance because of the failure of the investigators to realize that coagulation time varies with collision probabilities and that dilution without changing the electric character of the sol is possible only if the concentration of the precipitating electrolyte is maintained.

For example, in their work dilutions of a silver iodide sol were made with potassium iodide or silver nitrate so that the iodide ion concentration was maintained at a constant value.

METHODS OF PROCEDURE

Preparation of Hydrous Ferric Oxide Sols

Three methods were used for the preparation of the hydrous ferric oxide sols. These methods varied only as to the procedure of hydrolysis of a stock ferric chloride solution. The stock ferric chloride solution consisted of 270 grams of $FeCl_3 \cdot 6H_2O$ dissolved to make a liter of solution and allowed to stand for two weeks before using. The procedure of hydrolysis was then varied as follows:

Sol A. One hundred and forty milliliters of the stock ferric chloride solution was dropped at the rate of two drops per second into four liters of boiling distilled water; smaller batches were occasionally prepared, in which cases the same proportions were used. The sol was always prepared in an Erlenmeyer flask to minimize evaporation. The sol was allowed to stand until boiling stopped and was then immediately cooled under running tap water. The entire time of preparation including cooling was about an hour and a half. This sol will be referred to as the Sorum sol

since its preparation follows that used by Sorum (1928) and later modified as reported by Tuller and Eblin (1944).

Sol B. In this case the 140 milliliters of the stock solution of ferric chloride was dropped at the rate of two drops per second into four liters of boiling water under reflux conditions. In this preparation no water or hydrochloric acid formed in the process of the hydrolysis was lost through evaporation. The sol was cooled as above.

Sol C. This colloid was prepared by adding the above-mentioned quantity of ferric chloride all at once to boiling water under reflux conditions. The resulting preparation was then kept at about 104° C for one hour before cooling as above.

The sols produced by the above-mentioned methods of preparation are all positively charged and have a deep wine color. There was no evidence of sedimentation either immediately after preparation, after standing, or after reasonable periods of dialysis.

Purification of the Sols

During the course of the preparation of the colloid,

hydrochloric acid is formed and acts as a stabilizing electrolyte. Dialysis of the colloid removes the hydrochloric acid as a function of the period of dialysis. The colloid is said to be purified and the purity indicated as a function of the chloride content remaining in the sol. Since this investigation was undertaken to show the relationship of the purity of the sol and the coagulation value of the electrolyte as affected by the concentration of the colloid, the hydrous ferric oxide sol was dialyzed for varying periods of time.

The method used was an adaptation of Sorum's (1928) modification of Neidle's (1916) hot dialysis. The dialyzer consisted of two batteries of three one-liter, tall pyrex beakers placed in a large water bath. The temperature of the water bath was maintained at 58-62° C. Distilled water was allowed to flow through each beaker at a rate of about 500 milliliters per hour. An individual water supply was arranged for each beaker. The water was admitted at the bottom of each beaker and allowed to overflow into the water bath, which had an outlet to the drain.

The dialyzing membrane used was Visking Cellophane Sausage Casing and came in a number of sizes designated by the inflated diameter. The two sizes used were the 36/32" and the 1 5/8" tubes. After the cellophane casing was soaked in distilled water for an hour, a single knot was tied in one end and the other was fastened by means of Scotch tape to a

glass neck of slightly smaller diameter than the tubing. The system of membrane and glass support was then suspended in the dialyzer by copper wires attached to a horizontal glass rod above the dialyzer.

Any convenient volume of colloid could be purified, but as a rule the volume chosen was 250 milliliters, although occasionally batches as small as 150 milliliters were employed. Samples of the colloid were dialyzed for periods of time varying from 2 to 32 hours; a few samples were dialyzed as long as 5 days.

Evaporation and osmotic effects which might change the concentration of the colloid during dialysis were minimized by the use of a cork and capillary tube fitting into the glass neck holding the membrane. The cork effectively cut down the evaporation. The capillary tube extended into the colloid; any osmotic pressure developed was balanced by the hydrostatic pressure in the tube.

The usual method of indicating the purity of this colloid is the ratio of iron content to chloride content. Therefore analyses, described in a later section, were made of the iron and chloride contents of each sample.

Characteristics of the Dialytic Membranes

Characteristics of the cellophane membrane were determined to give an indication of the uniformity. Three

measurements, thickness of the membrane, the specific water content, and rate of flow of water (RFW), were made on samples taken at various points throughout the rolls used.

The thickness of the membrane was measured using a microscope with a calibrated eyepiece. The specific water content as defined by Elford (1931) is the ratio of the difference between the weight of a given area wet and that area dry to the wet weight.

$$\text{specific water content} = \frac{\text{wet weight - dry weight}}{\text{wet weight}}$$

This result may be made general by calculating it on the basis of the grams per square centimeter; that is, an area term is introduced into the denominator of the above equation. The area chosen for the specific water content determination was the same as that of the circles cut for the rate of flow of water determination. A circle was cut from the membrane, weighed dry, soaked for a given length of time, and weighed wet. The wet weight was determined immediately after placing the wet membrane between sheets of filter paper for an instant to remove excess moisture. Two periods of time were used for soaking, 1 hour and 24 hours.

The rate of flow of water was determined using the apparatus and method of Bauer and Hughes (1934). The apparatus consisted primarily of a 100-cm. glass tube made by extending the length of a 5-ml. microburet and a metal device

for holding the membrane. The RFW was determined by the following equation:

$$RFW = \frac{v\,\delta\,60,000}{APt}$$

where v is the volume in milliliters, δ is the membrane thickness in millimeters, A is the area of the orifice in square centimeters, P is the average pressure in centimeters, t is the time in minutes, and 60,000 is a conversion factor.

Although the above measurements are usually used with membranes to be employed in ultrafiltration and do not therefore indicate anything about the dialysis rates possible, they do serve to indicate the uniformity of the membrane.

The specific water content and RFW were found for membranes which had been soaked for 1 hour and for 24 hours. These times were chosen to correspond to the conditions under which the membranes were used; i.e., the membranes were soaked for an hour before use in the dialyzer and were in the dialyzer for periods of 2 to 32 hours. The RFW was calculated for two periods of time, 18 and 24 hours, and the average figure taken for purposes of comparison. Table 1 shows the results of the above determinations.

Table 1

Characteristics of the dialytic membranes

Membrane	Specific water content gms./sq.cm. 1 hr.	24 hrs.	Membrane thickness mm.	RFW cc./sq.cm./min. 1 hr.	24 hrs.
Lot 725 - 1 5/8"					
a	0.080	0.082	0.040	0.0017	0.0015
b	0.077	0.079	0.038	0.0016	0.0022
Lot 734 - 1 5/8"					
a	0.098	0.099	0.038	0.0026	0.0021
b	0.098	0.100	0.036	0.0023	0.0022
Lot 725 - 36/32"					
a	0.0090	0.0088	0.021	0.0029	0.0026
b	0.0090	0.0096	0.022	0.0029	0.0025

A membrane in contact with water for a considerable period of time might be expected to swell more than a membrane which had been soaked for a short time. If this greater swelling took place, the specific water content should increase slightly and the rate of flow of water decrease slightly. This occurred, as may be seen by a comparison of the data for the membranes which had been soaked for 24 hours and for those which had been soaked for only 1 hour. Samples taken from the same lot proved to be reasonably consistent in their characteristics, while some variations were shown with membranes from different lots. There was very little change in the RFW, which indicated that similar results in dialysis might be expected from two different lots.

Analysis for Iron

The method first tried in connection with this work was the orthophenanthroline-complex colorimetric method as described by Fortune and Mellon (1938). At first results were low; due probably to the high concentration of nitric acid used in dissolving the sample. The use of hydrochloric acid seemed to remedy this error for the most part. However, results still tended to be a little erratic as checked against gravimetric analysis. This method was therefore not considered adequate in its application to this problem.

Nichols, Kramer and Bailey (1932b) reported that the permanganate method and the thiocyanate colorimetric methods were not reliable. It is probable that the permanganate method was unsatisfactory because of the large amount of chloride that might be present. They used the Knop (1924) dichromate method for iron.

The analyses for this problem were finally made by a modified dichromate method. That is, the quantities of the chemicals used were modified so that the analysis could be done on a five milliliter colloid sample, using 0.05N dichromate solution and a microburet calibrated to 0.02 milliliter.

Analysis for Chloride

It was decided to use a nephelometric or turbidimetric type of analysis for the chloride ion since the ion concentration following prolonged dialysis would be extremely small. Three procedures employing silver nitrate were tested.

The photometer was used as an instrument for measuring turbidity. This procedure appeared to work successfully if the ion concentration was quite high, bordering on sedimentation limits for silver chloride; it was not satisfactory for very small chloride concentrations.

A nephelometric determination was tried using a Coleman universal spectrophotometer with a special nephelometric attachment. This procedure gave reproducible results. However, the scale range of only 10 per cent was not sufficiently accurate for reading unknown concentrations.

A Klett immersion nephelometer was used and proved to be satisfactory. Standard solutions of sodium chloride were prepared according to the method of Lamb et al. (1920). To a given volume of chloride solution there was added sufficient 95-per cent ethyl alcohol to make up a total volume of ten milliliters. To this solution were then added 5 milliliters of 0.8N nitric acid solution and 5 milliliters of 0.005N silver nitrate. The final solution was then placed in a constant temperature bath at 40° C for 35 minutes.

According to Lamb, the opalescence should not change over a period of 30 to 40 minutes following the above treatment. After the digestion period, the usual nephelometric technique was followed of putting some of the standard solution in both cups of the instrument. The left-hand solution was then set to read 20 on the scale and the right-hand side matched to it. The unknown solutions were then always placed on the left-hand side. The standards were chosen such that the unknown readings were never less than 15 nor greater than 25.

The unknown chloride concentration was calculated with the aid of Kober's (1913) formula,

$$Y = \frac{S}{X} - \frac{(1 - X)KS}{X^2}$$

where Y is the scale reading, S is the standard reading, X the ratio of the chloride concentrations, and K the nephelometer constant for the particular instrument and conditions used.

In making the analysis, the colloidal solutions were prepared by dissolving five-milliliter samples in 5 milliliters of 6N nitric acid. Depending upon the concentration of chloride present, 2 milliliters or less was taken for analysis. To the unknown solution was added sufficient water to make 5 milliliters of solution, to which were added 10 milliliters of alcohol and 5 milliliters of 0.005N silver nitrate. This solution was then treated as with the standards.

Determination of pH

Investigation was made of the pH of the hydrous ferric oxide sols used in order to relate pH to the purity of the colloid and to changes taking place upon aging.

The pH was determined both with a large Cameron meter and with a portable Coleman meter. As there seemed to be coagulation of the colloid by the potassium chloride used in the salt bridge of the Cameron pH meter, the bridge was modified by making use of a capillary tube such that the surface of potassium chloride exposed to the colloid was a minimum and no coagulation appeared to take place. Thereafter pH readings were reproducible.

Coagulation and Transmission of Light

One of the methods of following changes in a colloid upon aging and upon the addition of an electrolyte is to observe the change in light transmission. The instrument used in these studies was the KWSZ photometer manufactured by Wilkins-Anderson Company. This photometer consists essentially of a double cell, balanced bridge system using photoelectric cells and glass absorbent filters with a 100-watt lamp as a light source. The tubular cuvettes used were held in the instrument by adaptors placed on the carriage. The carriage was arranged so that either an unknown or standard

solution could be thrown into the beam of light. The filter chosen for this work was the #9 absorbing at 725 millimicrons. This filter gave the maximum light transmittancy for the hydrous ferric oxide sol.

The instrument was used for two purposes. First, the relationship of the transmission of light to the age and the concentration of the colloid was determined. Second, the process of agglomeration as a function of the change in light transmittancy was followed.

In using the instrument to measure the transmission of the sol in the first case mentioned above, the standard chosen was distilled water, which was the dispersion medium of the sol. Since water was to be considered as 100 per cent transmittant, any decrease in transmittancy was due to the presence of the colloid. The per cent transmission could be read directly from the potentiometer of the instrument.

In following the change of transmission of light, with agglomeration of the colloid, a slightly different procedure was used. With agglomeration the interest lies in the change of transmission compared to the original colloid. Therefore the standard used was the colloid diluted to the appropriate concentration with distilled water. The per cent transmission of the agglomerating colloid was noted each minute for the first five and every five minutes thereafter until coagulation took place.

Since it is well known that a difference in the method of mixing the colloid and the coagulating electrolyte will cause a difference in the agglomerating behavior, an attempt was made to use a uniform method of mixing. The procedure followed was to add to the colloid a sufficient quantity of electrolyte to make the total volume 5 milliliters. The mixture was immediately stirred and placed in the instrument. The first reading of transmission of light was taken thirty seconds after the addition of the electrolyte.

The choice of the amount of colloid used was on the basis of the final concentration desired. For example, if a 50 per cent dilution was to be used, 2.5 milliliters of electrolyte was added to 2.5 milliliters of the colloid. The usual concentrations of colloid employed were 20, 40, 50, 60, and 80 per cent, although in some cases concentrations as low as 5 per cent were used.

RESULTS AND DISCUSSION

Properties of the Sols

Investigation was made of some of the similarities and differences of the colloids resulting from the three methods of preparation of hydrous ferric oxide. All three methods gave fairly reproducible colloids, as may be seen from the data on pH and per cent transmission given in Table 2. Samples of colloid prepared in like manner give like pH and transmission measurements. The differences in transmission among the three colloids are those that might be expected from the methods of preparation. That is, the C colloid is the most transmittant and the A colloid the least. Since the A colloid was prepared by dropping ferric chloride solution into boiling water, evaporation and completeness of hydrolysis would tend to make it optically more dense than either the B or the C colloid prepared under reflux conditions. The difference in dropwise hydrolysis and that occurring when all the ferric chloride was added at once showed itself in the transmission changes of the B and C colloids.

Table 2

Per cent transmission and pH of freshly prepared and aged colloids

Sol	pH (time of aging) none	pH (time of aging) 3 months	% Transmission (time of aging) none	% Transmission (time of aging) 3 months
A_3	1.10	1.15	60.2	74.5
A_4	1.30	1.10	59.6	68.5
B_3	1.00	1.05	64.0	75.0
B_4	1.10	1.05	64.2	74.0
C_3	1.20	1.30	70.4	83.0
C_4	1.10	1.05	70.2	81.5

As might be expected, aging effects were also different. Table 2 also shows the pH and per cent transmission for the colloids after they had been aged for about 3 months. The C colloid showed a much greater increase in transmission of light with aging than did either the B or the A sol. Fuks and Rabinerson (1936) and Nichols et al. (1932b) have pointed out the possibility of a reversal of hydrolysis in which ferric chloride is reformed. Since such a reversal would cause the observed increase in light transmission by the colloid, investigation was made of the content of the ionic iron before and after aging. Examination of the data in Table 3 shows that the B and C colloids show a definite increase in the ionic iron content, whereas the A colloid shows

a definite decrease. This behavior of the C colloid is in agreement with the work of Nichols et al. (1932b) and shows that differences in method of preparation will cause differences in behavior of presumably the same colloid.

Table 3

Ionic iron content
(gms. per liter)

Sol	Iron (time of aging) none	3 months
A_3	0.08	0.00
A_4	0.20	0.01
B_3	0.20	0.40
B_4	0.24	0.45
C_3	0.25	0.60
C_4	0.20	0.45

Later it will be shown that the differences in the three colloids are even more apparent in their behavior toward added electrolytes. These differences are also shown by one other characteristic, their behavior in dialysis. Table 4 gives data on the iron and chloride content of the various sols used. In the last column is given the purity (P) of the colloid in terms of the ratio of the equivalents of iron to the equivalent of chloride per liter. Examination of the data for the A_3, B_3, and C_3 sols shows that the C sol behaves

Table 4

Relationship of the purity (P) to the time of dialysis of several sols

(P = equivalents of Fe/equivalents of Cl)

Sol	Hrs. of dialysis	Fe content gms./liter	Cl content gms./liter	P
A_3	0	2.27	6.42	0.7
	2	2.16	1.33	3.1
	4	2.13	0.57	7.2
	6	2.13	0.19	21.3
	8	2.09	0.14	28.5
	10	2.11	0.085	47.4
	12	2.10	0.060	67.0
	14	2.14	0.028	147
	16	2.11	0.034	118
	18	2.13	0.021	194
	20	1.93	0.017	217
	22	2.14	0.023	178
	24	1.98	0.015	253
	30	2.31	0.013	348
B_3	0	1.86	4.58	0.8
	2	1.82	1.15	3.1
	4	1.80	0.36	9.6
	6	1.80	0.21	16.4
	8	1.77	0.09	19.8
	10	1.86	0.047	39.5
	12	1.75	0.028	71.0
	14	1.80	0.024	123
	18	1.90	0.018	152
	20	1.78	0.010	190
	24	1.77	0.006	340
C_3	0	1.79	5.22	0.7
	4	1.76	1.00	3.4
	8	1.80	0.19	18.2
	10	1.76	0.15	22.4
	14	1.70	0.10	32.0

(continued)

Table 4 (continued)

Sol	Hrs. of dialysis	Fe content gms./liter	Cl content gms./liter	P
C_3 (cont.)	16	1.69	0.122	26.5
	18	1.76	0.092	36.6
	20	1.87	0.106	33.8
	24.5	1.74	0.018	182.0
A_5	0	2.08	5.32	0.7
	2	1.86	1.32	2.7
	6	1.87	0.24	14.7
	8	1.88	0.14	25.6
	10	1.77	0.072	47.0
	12	1.86	0.058	62
	14	1.81	0.029	119
	16	1.82	0.033	105
	20	1.98	0.025	151
	24	2.00	0.016	262
	28	2.18	0.008	510
	32	1.91	0.009	405
A_6	0	1.94	4.680	0.8
	2	1.91	0.935	3.9
	6	1.91	0.138	26.5
	8	1.82	0.095	31.7
	10	1.86	0.062	57.2
	14.5	1.91	0.035	104
	16	1.82	0.027	129
	20	1.86	0.024	147
	24	1.87	0.011	325
	28	1.89	0.009	400
	32	1.90	0.012	305
A_7	0	2.00	4.060	0.9
	2	1.90	0.935	3.9
	6	1.87	0.124	28.9
	8	1.90	0.090	40.6
	10	1.89	0.060	60.3

(continued)

Table 4 (continued)

Sol	Hrs. of dialysis	Fe content gms./liter	Cl content gms./liter	P
A_7 (cont.)	12	1.81	0.043	80
	14	1.88	0.031	114
	16	1.81	0.025	141
	20	1.85	0.018	201
	24	1.89	0.012	300
	28	1.86	0.0075	475
	31	1.86	0.0070	508
A_8	2	1.81	0.976	3.5
	6	1.84	0.131	26.9
	10	1.86	0.068	52.2
	12	1.80	0.032	111.0
	14	1.80	0.033	99.0
	20	1.90	0.017	214
	24	1.86	0.012	296
	28	1.90	0.0056	649
	32	1.92	0.0090	409

quite differently from either the $\underline{A}_3$ or the $\underline{B}_3$ sol, because the loss of chloride by dialysis is very slow. The B colloid holds its chloride content somewhat more tenaciously than does the A but not nearly so strongly as the C sol. All of the A sols, however, lose the chloride content by dialysis at about the same rate. The A sols are the ones which were used most extensively in the studies on coagulation.

As previously mentioned, the colloids were dialyzed under circumstances designed to give the minimum differences in concentration of the hydrous ferric oxide. That this was successful is shown by the reasonable agreement of the iron contents of the samples in any given colloid series.

As a rule, the period of dialysis is an indication of the purity of a sample in any given colloidal series. Since however, there are some discrepancies, such as the last of the $\underline{A}_6$ series in which the sample dialyzed for 28 hours has a smaller chloride content than the 32-hour sample, all colloids will hereafter be referred to in terms of the purity (P) as designated in Table 4. In general, however, the greatest change in chloride content occurs within the first 6 to 10 hours of dialysis and then gradually tapers off. Colloids of the A and B series dialyzed as long as 36 hours gave no test for chloride ion under the conditions of the nephelometric determination and when dialyzed for 51 to 72 hours finally showed signs of partial sedimentation. A colloid of the C

series which was dialyzed for a little over 5 days showed a chloride analysis of 0.0139 gram per liter with no sign of sedimentation either immediately or after aging for 3 months. This is in line with other information showing that the chloride in the C colloid is held especially tightly.

The effect of dialysis on the stability of the three preparations of hydrous ferric oxide is shown in the pH and transmission data given in Table 5.

Table 5

Per cent transmission and pH of dialyzed sols

Sol	pH (time of aging)		% Transmission (time of aging)	
	none	3 months	none	3 months
A_3 (P = 21.3)	2.4	2.5	54.5	54.0
A_3 (P = 147)	3.8	3.8	54.6	55.0
A_3 (P = 253)	5.4	5.2	56.0	56.0
B_3 (P = 152)	4.4	3.9	58.0	58.0
B_3 (P = ∞)	5.8	4.4	59.0	59.0
C_3 (P = 21.7)	3.3	3.4	65.5	65.5

Again the behavior of the three different colloids varied with aging. In all three cases the per cent transmission remained the same, contrary to the non-dialyzed sols discussed previously, but the pH change was different. In the case of the C_3 colloid, there was a slight increase in pH

while the B_3 colloids showed definite decrease and the A_3 sols changed little if at all.

Agglomeration and Coagulation

There is extensive literature on the collision and adhesion of colloidal particles. This phenomenon has been called agglomeration, flocculation, or coagulation. During the course of this investigation, it was decided that a distinction must be made between growth in particle size and the point at which growth is sufficient so that sedimentation will ultimately result. The term agglomeration, therefore, is used throughout to refer to the collision and adhesion of colloidal particles whether or not sufficient particle size is reached such that sedimentation follows. The term coagulation is used to refer to the final stage of agglomeration which ultimately will result in sedimentation.

The progress of agglomeration may be followed by any method which measures a physical change accompanying the growth in particle size. The change in transmission of light was used in this investigation and was followed by means of the KWSZ Photometer. As agglomeration takes place, absorption of light increases, causing a decrease in the intensity of light striking a photoelectric cell. This change in transmission was recorded as the per cent transmission at a given time. Thus the complete course of agglomeration could

be followed as a function of transmission and time until coagulation, and finally sedimentation, resulted.

The transmission for a given sol decreases with agglomeration until coagulation occurs, after which the transmission increases. The second phase of this change in transmission was dependent upon the rapidity or slowness of sedimentation following coagulation. Usually the slower the sedimentation, the slower the increase in transmission.

Wannow (1936) and others have mentioned that the curves of opacity or per cent transmission plotted against time have shown an upward trend or decrease of opacity and increase of transmission following the original course of the change. However, these investigators have concerned themselves either with actual transmission measurements taken from the first half of the curve or with data useful for studying the kinetics of agglomeration obtainable from the rate of change of transmission. They have failed for the most part even to indicate the full course of the change in transmission or opacity and did not explore the possibilities of the change in slope of the transmittancy-time curves.

As previously mentioned, Troelstra and Kruyt (1943) have pointed out that the effects of agglomeration and any resultant coagulation should be identified separately from sedimentation effects. Since the rate of sedimentation depends on the type of coagulum formed, studies of the kinetics of agglomeration and coagulation should be dissociated from

sedimentation effects. The same thing is also true in making determinations of the coagulation values of electrolytes.

The change in slope involved in following the course of agglomeration was investigated as a possible indication of coagulation. Table 6 and Figure 1 show the data and graphs obtainable when the per cent transmission of an agglomerating colloid is followed as a function of time. The concentration of the colloid in the final solution is indicated in terms of volume. The per cent transmission is observed to decrease more or less rapidly as agglomeration progresses. The reversal of the direction of change of transmission, as indicated by the upward trend in the curve, occurs at the point of coagulation. The sharpness of the slope or rapidity of the increase of transmission is indicative of the rate of sedimentation following coagulation. When cuvettes were removed from the instrument at the instant of change of direction, no sedimentation was observable. Sedimentation sufficient to show two to three millimeters of clear supernatant liquid occurred from 15 seconds to several hours following the break in the curve. Flocs, visible particles, were observed in every case. For convenience, the time at which the break occurs has been denoted as the critical time or t_c. The critical time, therefore, is the time of coagulation, i.e., when agglomeration is complete but sedimentation has not yet occurred.

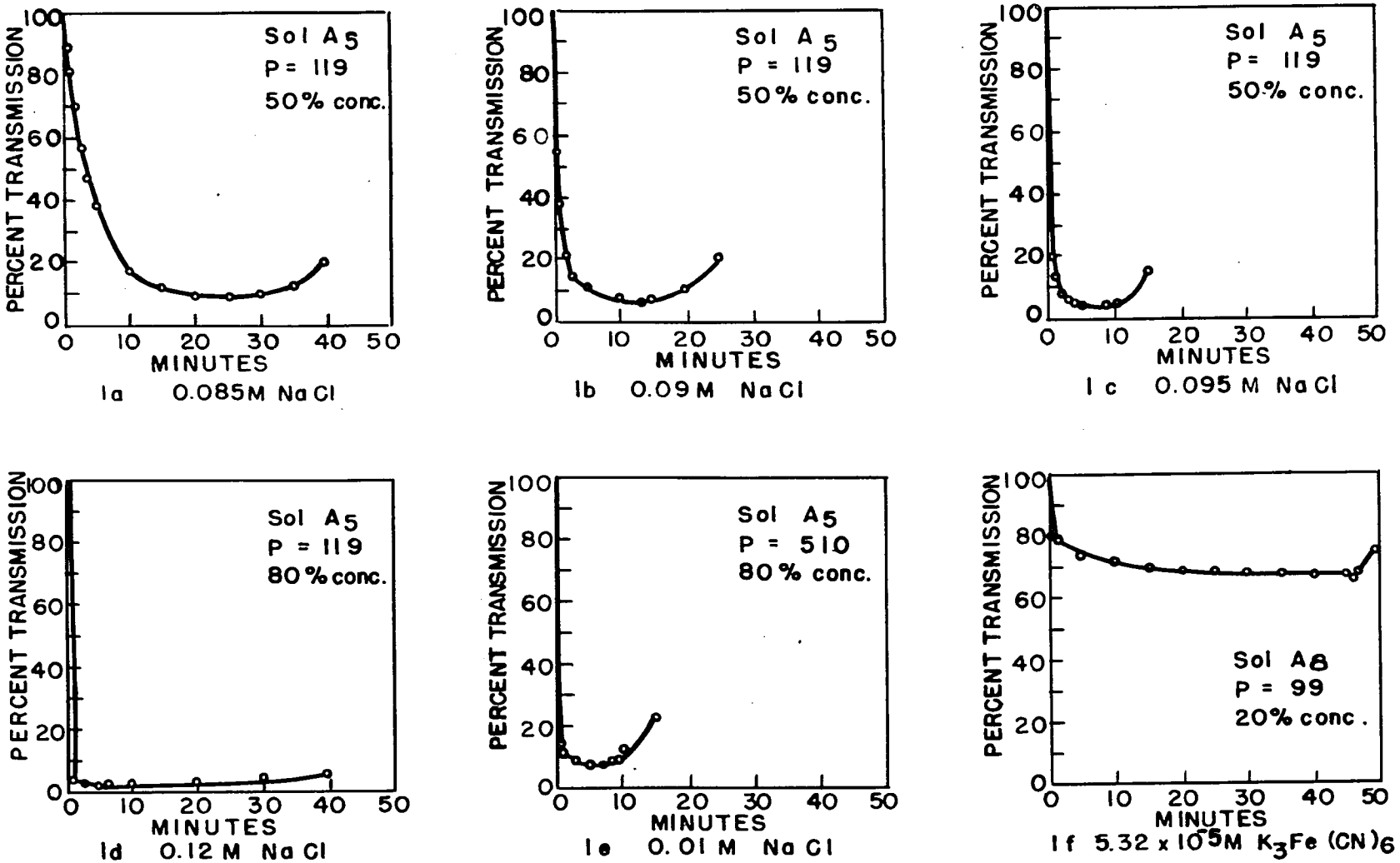


Fig. 1 Percent transmission of agglomerating sols as a function of time.

Table 6

Per cent transmission of agglomerating sols as a function of time

Sol	Electro-lyte	% Trans-mission	Time min.	Critical time min.
A_5(50%, P = 119)	0.085 M NaCl	88.0	0.5	
		81.0	1	
		70.0	2	
		57.0	3	
		47.0	4	
		38.0	5	
		17.0	10	
		11.5	15	
		9.5	20	
		9.0	25	25
		9.1	26	
		9.5	30	
		12.0	35	
		20.0	40	
A_5(50%, P = 119)	0.09 M NaCl	55.0	0.5	
		38.0	1	
		21.0	2	
		14.0	3	
		10.2	5	
		7.3	10	
		6.6	14	14
		6.7	15	
		10.0	20	
		20.0	25	
A_5(50%, P = 119)	0.095 M NaCl	20.0	0.5	
		13.0	1	
		7.5	2	
		6.2	3	
		5.4	4	
		5.0	5	
		4.6	9	9
		4.7	10	
		15.0	15	

(continued)

Table 6 (continued)

Sol	Electro-lyte	% Trans-mission	Time min.	Critical time min.
A_5(80%, P = 119)	0.120 M NaCl	3.5	0.5	
		2.0	3	
		2.0	5	
		2.1	7	6
		2.2	10	
		3.0	20	
		4.0	30	
		5.0	40	
A_5(80%, P = 510)	0.01 M NaCl	14.0	0.5	
		11.5	1	
		10.0	2	
		9.0	3	
		8.2	4	
		7.8	5	
		7.4	6	
		7.4	8	8
		8.0	9	
A_8(20%, P = 99)	5.32×10^{-5}M $K_3Fe(CN)_6$	80.0	0.5	
		79.5	1	
		74.0	5	
		72.0	10	
		70.0	15	
		69.0	20	
		68.3	25	
		67.8	30	
		67.5	35	
		67.2	40	
		67.2	45	
		66.0	46	46
		67.0	47	

The series of graphs in Figure 1 illustrates the types of changes of light transmission that take place when an electrolyte is added to a colloid. Figures 1-a through 1-c show the changes in the transmission as the critical time or coagulation is reached more rapidly. It should be noticed that as the critical time becomes smaller the rate of change of transmission becomes greater. This indicates not only that agglomeration is more rapid but that sedimentation takes place more rapidly. This very general statement is most accurately applied to colloids differing only in concentration of the added electrolyte.

The concentration and purity of the colloid affect the critical time and the rate of sedimentation. For example, the data in Table 6, as illustrated in Figure 1-d and 1-e, show Sol $\underline{A}_5$ of 80 per cent concentration and two different degrees of purity. If the data and figures for Sol $\underline{A}_5$ (80%, $\underline{P}$ = 119) are compared with those for Sol $\underline{A}_5$ (50%, $\underline{P}$ = 119), Figures 1-a to 1-c, it is found that the per cent transmission does not increase as rapidly following coagulation as it does in any of the 50-per cent colloids; also the more pure, concentrated colloid, Sol $\underline{A}_5$ (80%, $\underline{P}$ = 510), shows a sharper change than does the less pure. These differences are due to the different types of coagulum formed and hence to changes in the rate of sedimentation. In the case of Sol $\underline{A}_5$ (80%, $\underline{P}$ = 119), the rate of change of light transmission during

agglomeration is very rapid and the critical time is short; yet the increase in transmission is very slow. When examined, this colloid showed a granular, dense coagulum which settled very slowly. This is in contrast to the flocculent, massive, rapidly settling coagula of Sol $\underline{A}_5$ (50%, $\underline{P}$ = 119). The coagulum of the highly concentrated sol becomes more massive and flocculent as purification proceeds and hence settles more rapidly, as indicated in Figure 1-e.

If the colloid is of such nature that coagulation causes a tendency toward gelation, the critical time is frequently indicated by a sharp decrease in transmission before a rapid increase. This is illustrated by the data and graph for Sol $\underline{A}_8$ (20%, $\underline{P}$ = 99) when the sol was coagulated with potassium ferricyanide. The sharp decrease is due to a sudden packing effect occurring at the coagulation point and before sedimentation takes place. This was typical of most of the coagulation obtained with potassium ferricyanide. The colloid preparation denoted as Sol $\underline{B}$ showed this tendency particularly in the higher sol concentrations. Sol $\underline{C}$ at first acted like Sol $\underline{B}$, until coagulation ultimately produced gelation such that there was just a steady decrease in transmission until sedimentation was nearly complete. In other words, the decrease in transmission was due to agglomeration and the packing following coagulation but gave no indication of the coagulation point. The critical time, therefore, can

be determined only on colloids not showing gelation tendencies upon coagulation and is indicative only of the time needed for coagulation, not of the type of coagulum or rate of sedimentation.

In determining the per cent transmission-time data, the phenomenon of autocatalysis was apparent in only a few cases. As Patel and Desai (1930) have pointed out, the presence of autocatalysis and the resultant S-curve is dependent on a number of factors among which are the concentration of the added electrolyte, the purity of the colloid and the concentration of the colloid. None of the A or B colloids exhibited autocatalysis for any concentration of electrolyte. The C sol did show a slight tendency toward autocatalysis. Table 7 gives some data on the per cent transmission as a function of time of the agglomerating colloid where autocatalysis was exhibited. Examination of the data for Sol C_3 (P = 26.5) shows that the per cent transmission changes slowly with time and then rapidly and finally levels off before coagulation occurs. This is typical of the S-shaped function. The data for various electrolyte concentrations added to Sol C_3 (80%, P = 21.7) show that with increasing concentrations of electrolyte there is a decrease in the S-shaped function; the per cent transmission changes rapidly with time.

Table 7

Per cent transmission as a function of time for an agglomerating sol showing autocatalysis

Sol	Conc. of NaCl molar	% Transmission	Time min.
C_3 (80%, P = 26.5)	0.056	88.0	0.5
		86.0	1
		82.0	2
		78.0	3
		74.0	4
		69.0	5
		46.0	10
		34.0	15
		29.5	20
		28.3	25
		27.3	28
		27.5	29
C_3 (60%, P = 26.5)	0.056	98.0	0.5
		97.0	1
		96.0	2
		94.0	3
		92.3	4
		90.0	5
		77.0	10
		62.0	15
		51.0	20
		45.0	25
		42.4	30
		41.3	35
		41.3	37
		41.5	38
C_3 (80%, P = 21.7)	0.08	95.0	0.5
		94.0	1
		92.0	2
		90.0	3
		84.0	5

(continued)

Table 7 (continued)

Sol	Conc. of NaCl molar	% Trans-mission	Time min.
C_3 (80%, P = 21.7) (continued)	0.08	63.0	10
		43.0	15
		29.0	25
		27.0	30
		24.0	33
		25.0	34
C_3 (80%, P = 21.7)	0.10	94.0	0.5
		93.0	1
		91.0	2
		83.0	4
		79.0	5
		50.5	10
		33.5	15
		28.0	20
		25.6	25
		25.0	26
		24.0	27
		25.0	28
C_3 (80%, P = 21.7)	0.12	27.0	0.5
		14.0	2
		13.2	3
		13.0	4
		12.7	5
		12.4	10
		12.3	15
		12.1	20
		12.0	24
		12.5	25

Kinetics of Coagulation and the Critical Time

As previously mentioned, coagulation phenomena are usually divided into two types, rapid and slow. Rapid coagulation is usually characterized by a rapid attainment of complete agglomeration followed by quick sedimentation and is produced by relatively high concentrations of a given electrolyte. Slow coagulation, on the other hand, is attained by relatively low concentrations of electrolytes, and slow sedimentation follows complete agglomeration. These, however, are merely qualitative indications of the rate of coagulation and, as has been seen in the earlier discussion, are not always adequate. That is, under certain circumstances, high concentrations of electrolytes may produce rapid and complete agglomeration but sedimentation is relatively slow.

The use of the critical time, determined in transmission studies, gives another means of differentiating between rapid and slow coagulation. Asterisks in Table 8 and Figure 2 indicate that part of the relationship between critical time and the concentration of added electrolyte which is an exponential function of concentration of electrolyte. The deviation from the exponential function which occurs with very rapid coagulation, i.e., when the critical time is short, may be due to limitations of the method rather than to any difference of behavior of the colloid. The high-valued

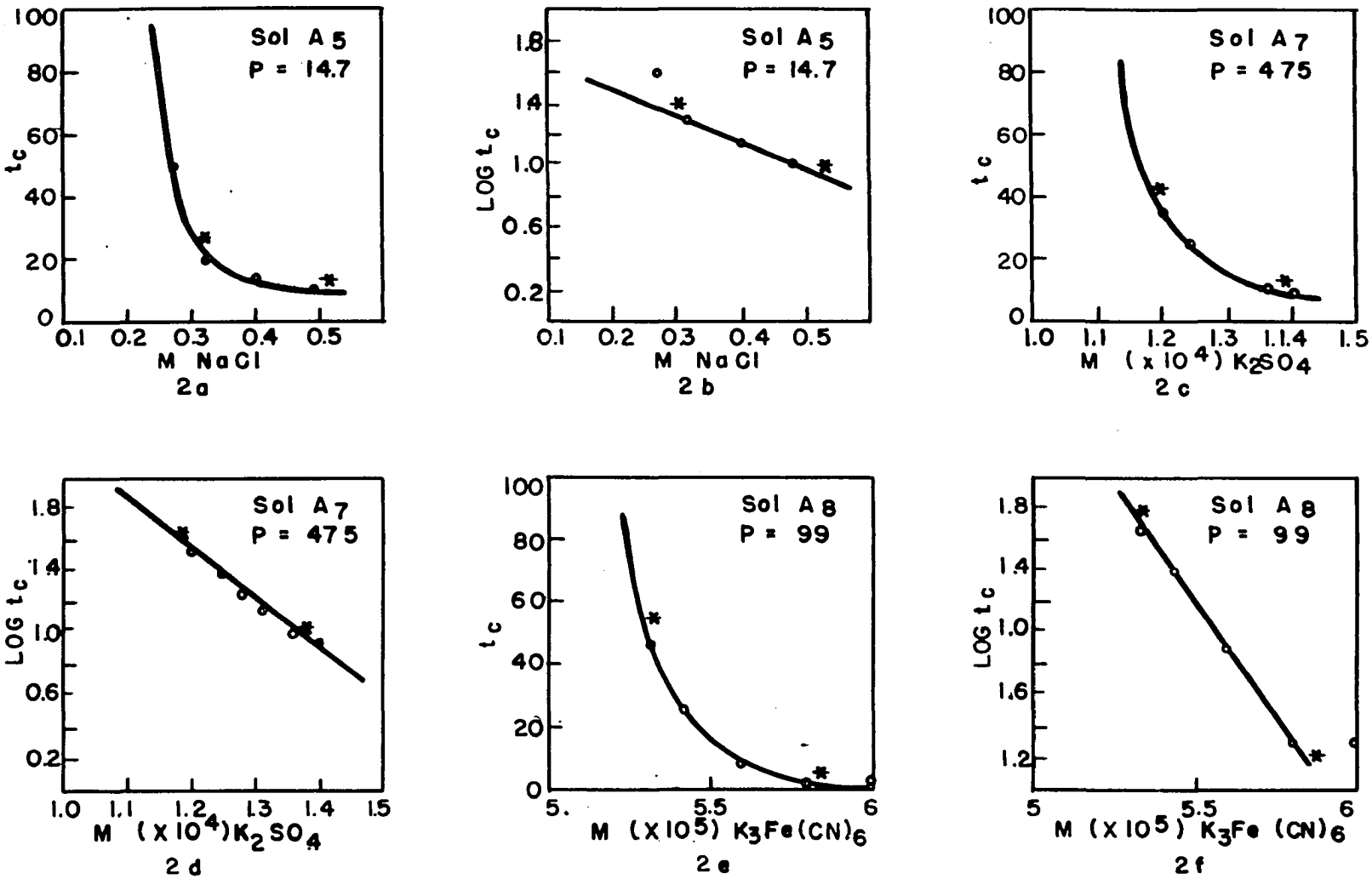


Fig. 2 Critical time (t_c) as a function of the molarity of electrolyte for sols of 20 ‰ concentration and purity (P) as indicated.

Table 8

Critical time as a function of the concentration of electrolyte for sols of 20 per cent concentration and purity (P) as indicated

Sol	Concentration of electrolyte molar	t_c min.	log t_c
A_5 (P = 14.7)	0.272 NaCl	49	1.60
	*0.32	19	1.28
	0.40	14	1.15
	*0.48	10	1.00
A_7 (P = 475)	*1.2 x 10^{-4} K_2SO_4	35	1.54
	1.248 x 10^{-4}	25	1.40
	1.28 x 10^{-4}	18	1.25
	1.31 x 10^{-4}	14	1.15
	*1.36 x 10^{-4}	10	1.00
	1.40 x 10^{-4}	9	0.95
A_8 (P = 99)	*5.32 x 10^{-5} $K_3Fe(CN)_6$	46	1.66
	5.43 x 10^{-5}	25	1.40
	5.6 x 10^{-5}	8	0.90
	*5.8 x 10^{-5}	2	0.30
	6.0 x 10^{-5}	2	0.30

critical times not falling within the exponential function, however, are due to slow coagulation. In other words, the extent of the rapid coagulation is indicated by the extent of the exponential function, while the slow coagulation is indicated by critical times too long to be included in the straight-line relationship.

The range of critical times, over which the exponential function was applicable, varied with the electrolyte used. For example, the length of the straight-line function is shorter for the univalent electrolytes, as exemplified by sodium chloride, than it is for potassium sulfate and potassium ferricyanide. As may be observed from the data in Table 8 and other data to be presented later, the critical times for the univalent electrolytes extend at the most from 5 to 35 minutes, while those for potassium sulfate and potassium ferricyanide have ranged from 3 to 50 minutes. In other words, the zone of rapid coagulation is greater for polyvalent electrolytes than for univalent electrolytes.

Burton-Bishop Rule and Critical Times

The critical time, discussed in the previous sections, was used as a criterion for coagulation in making the investigation of the relationship of the concentration of a hydrous ferric oxide sol, the purity of the sol with respect to the chloride ion concentration, and the coagulation value

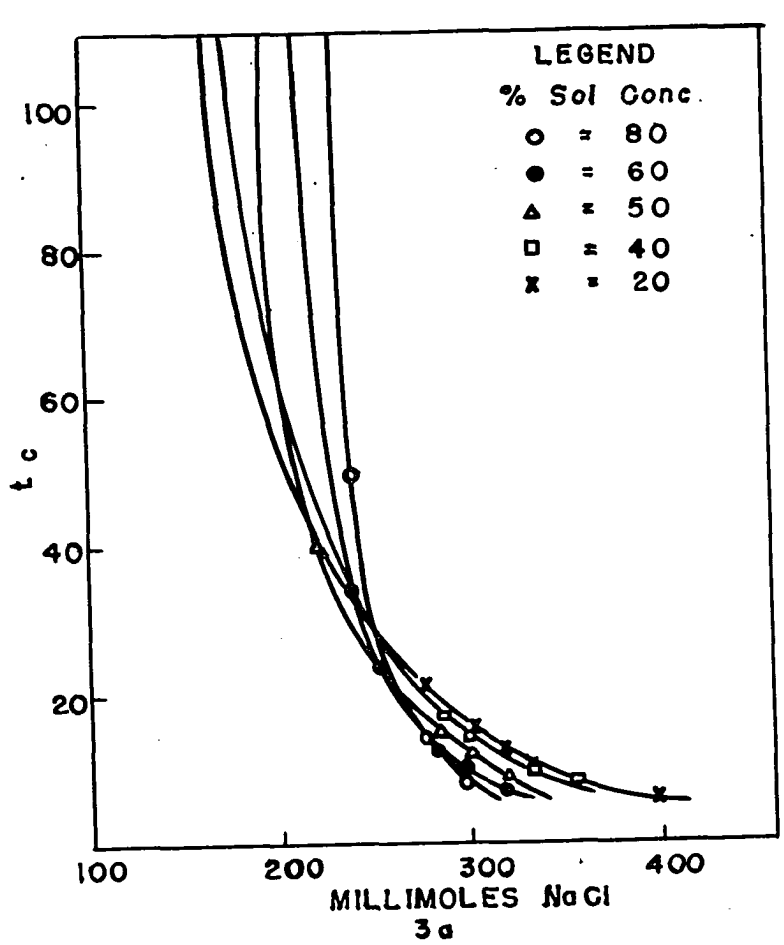
of an added electrolyte. The majority of the work was done in the region of rapid coagulation, i.e., the region in which the critical time is an exponential function of the concentration of electrolyte. The similarities and differences in slow and rapid coagulation were shown and will be discussed later.

Several critical times were determined for each concentration of the sol, and data were obtained for three to six different concentrations for each sol purity. Both an iron analysis and a chloride analysis were made on each sol sample, thus allowing a quantitative measurement of the purity of the colloid. The purities (P) are listed in Table 4, pages 41-43.

Coagulation studies were made on the three different sols, A, B, and C. Since Sol A was prepared by Sorum's (1928) method and is most like that commonly used in the previous investigations of the Burton-Bishop rule, it was the sol chosen for the most extensive investigation in this study.

The electrolytes used were sodium chloride, potassium chloride, potassium sulfate, and potassium ferricyanide. Sodium chloride was employed in the study of all three sols while the potassium salts were used only with Sol A.

Table 9 and Figure 3 show data and graphs giving the relationship of the concentration of electrolyte and the critical times for several concentrations of Sol A_5 (P = 47).



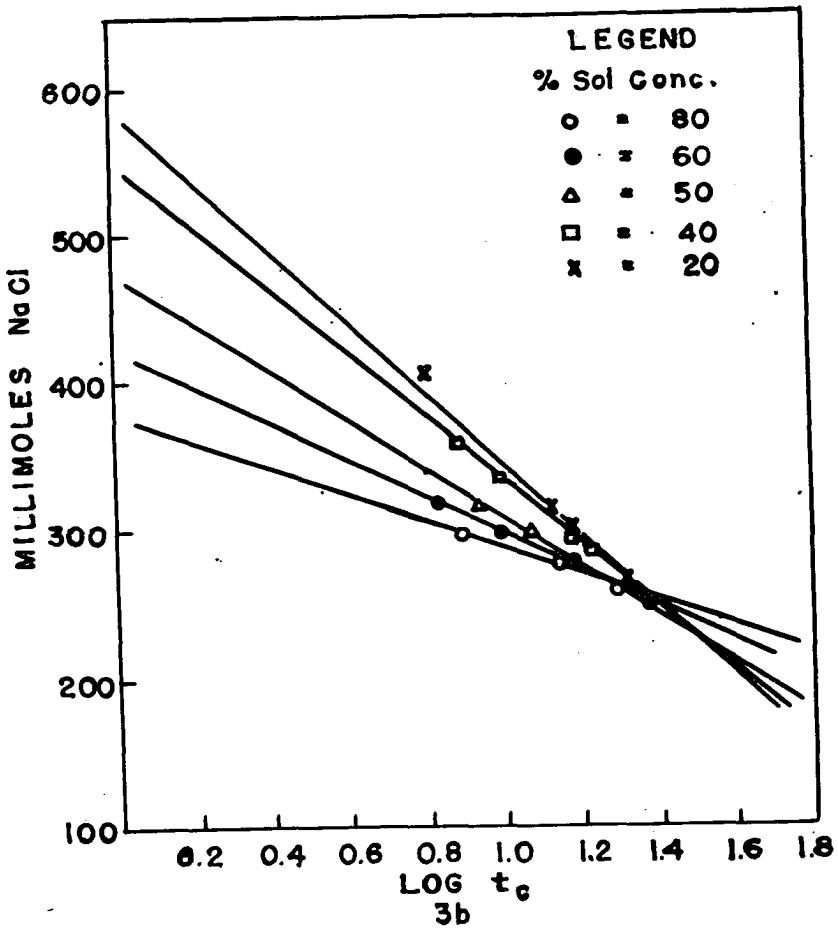


Fig. 3 Critical time as a function of the concentration of NaCl for Sol A_5 (P = 47) at several concentrations.

Table 9

Critical time as a function of the concentration of NaCl for Sol $\underline{A}_5$ ($\underline{P}$ = 47) at several concentrations

% Conc. of sol	Conc of NaCl millimoles/l.	t_c min.	log t_c	m	b
20	150	limiting value			
	240	30	1.48		
	*272	22	1.32		
	304	15	1.18		
	320	13	1.11		
	400	6	0.77	-24.5	590
40	170	limiting value			
	240	35	1.54		
	*288	17	1.23		
	300	15	1.18		
	336	10	1.00		
	360	8	0.90	-21.2	550
50	190	limiting value			
	200	40	1.85		
	*260	20	1.30		
	280	15	1.18		
	300	12	1.08		
	320	9	0.95	-16.2	475
60	210	limiting value			
	240	34	1.53		
	*254	24	1.38		
	286	15	1.18		
	300	10	1.00		
	320	7	0.84	-125	425
80	230	limiting value			
	240	50	1.70		
	*260	23	1.36		
	280	14	1.15		
	300	8	0.90	-88	380

The straight lines derived from the exponential function of the critical times and the coagulation value of the electrolyte tend to intersect at a point, as shown in Figure 3-b. This intersection of straight lines is typical of the coagulation behavior with univalent electrolytes except when the order of the coagulation values for the different concentrations is scrambled or when the purity of the colloid is extremely high. These exceptions will be discussed later.

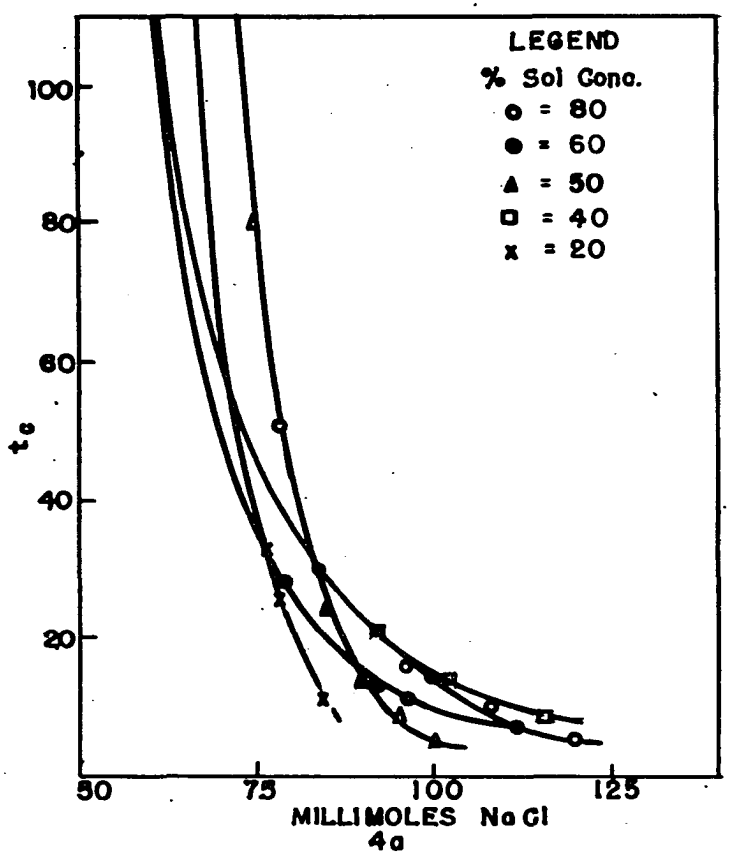
In order that coagulation values of the electrolyte for various concentrations of a given sol might be more easily compared, the intercept b of each line with the y-axis was determined. The numerical order of these intercepts is that of all of the coagulation values up to a point of intersection for a sample of the colloid. Hereafter, the intercepts are given in the tables as in Table 9 as b, the coagulation value in millimoles per liter at a critical time equal to one minute. These coagulation values are purely theoretical, since it was not possible to determine a value at a critical time of one minute, but the order is a valid means of indicating the relative values up to a point of intersection. For example, the order of the coagulation values of Sol A_5 (P = 47) as read from the graph of Figure 3-b or Table 9 shows an increase in the coagulation of sodium chloride for a decrease in concentration of the sol. The slope m was also determined by the equation for a straight line

$$c = m \log t_c - b$$

where c equals the concentration of the electrolyte.

The point of intersection may lie within, or just at, the edge of the zone of rapid coagulation. If it lies within the zone of rapid coagulation, the concentrations of electrolyte in slow coagulation will be in the inverse order to that indicated by the intercept $\underline{b}$. If the point of intersection is at the end of the zone of rapid coagulation, the order of the coagulation values may be, but are not necessarily, in the reverse order as in rapid coagulation. Figure 3-a shows graphically the relation between slow and rapid coagulation for various concentrations of Sol $\underline{A}_5$ ($\underline{P}$ = 47). The intersection of these lines illustrates a case in which slow coagulation is the inverse of rapid coagulation. In Table 9 the asterisk indicates the demarcation between the rapid and slow coagulation values. In all cases at least one slow coagulation value and a limiting value are given. The limiting value is that concentration of the electrolyte which will just produce agglomeration of the colloid as indicated by a steadily decreasing transmission value upon addition of the salt.

Figure 4 illustrates one of the exceptions to an orderly progression of coagulation values. This case shows the relationship of coagulation values to concentration of the colloid when the coagulation values are not varying directly with or conversely to the concentration of the colloid. As shown in Figure 4 and in Table 10, the decreasing order of the coagulation values in the most rapid coagulation is with



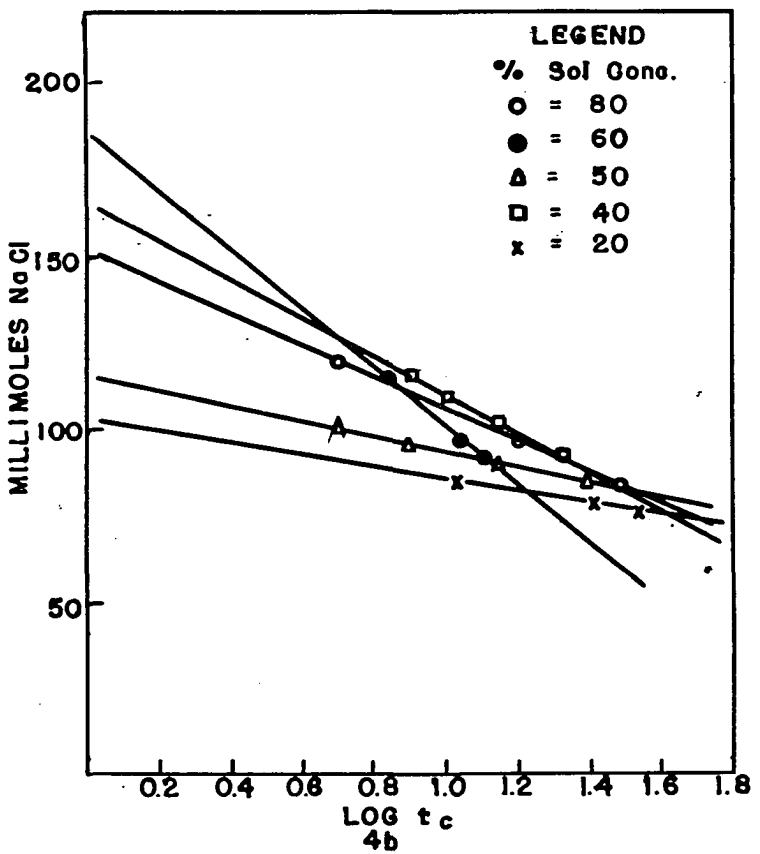


Fig. 4 Critical time as a function of the concentration of NaCl for Sol A_5 (P=119) at several concentrations.

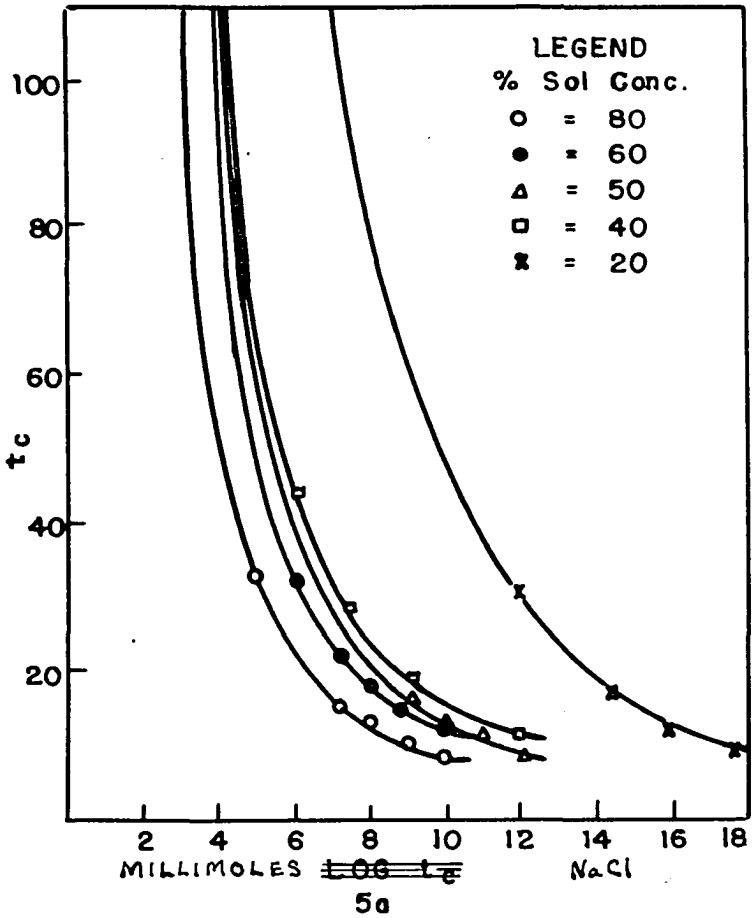
Table 10

Critical time as a function of the concentration of NaCl for Sol $\underline{A}_5$ ($\underline{P}$ = 119) at several concentrations

% Conc. of sol	Conc. of NaCl millimoles/l.	t_c min.	log t_c	m	b
20	65.0	limiting value			
	70.0	65	1.81		
	*76.8	33	1.52		
	78.4	26	1.41		
	85.0	11	1.04	-19.0	101
40	60	limiting value			
	70	60	1.78		
	*82	21	1.32		
	102	14	1.15		
	108	10	1.00		
	116	8	0.90	-48.5	165
50	70	limiting value			
	75	80	1.90		
	*85	25	1.40		
	90	14	1.15		
	95	9	0.95		
	100	5	0.70	-21.5	115
60	60	limiting value			
	77	28	1.45		
	*92	13	1.11		
	96	11	1.04		
	112	7	0.84	-81.0	184
80	70	limiting value			
	78	51	1.71		
	*84	30	1.48		
	96	16	1.20		
	100	14	1.15		
	120	5	0.70	-43.5	150

concentrations of Sol $\underline{A}_5$ ($\underline{P}$ = 119) of 60, 40, 80, 50, and 20 per cent. The order of the coagulation values in the slow coagulation as indicated by the limiting values is not the exact inverse but decreases with the concentration in the order of 80, 50, 20, 40, and 60 per cent. This scrambling of values occurs when partial purification of the colloid takes place. Its relation to a complete series of sols of different purities will be discussed later. In any case in which the scrambling takes place, the intersection of lines never occurs so nearly at a common point as in other cases in which the lines do intersect.

Figure 5 shows graphically an exception to the intersection of lines. When a sol in a given series has been purified sufficiently, there is a tendency for the exponential functions for the different concentrations to become parallel. Not only the logarithm of critical time as a function of the concentration of sodium chloride and the concentration of the sol, but also the relationship of the critical time to the coagulation values and to the concentration of the sol, show no intersection as far as the limiting value of the electrolyte is concerned. That is, the order of the coagulation values with respect to the concentration of the sol is the same irrespective of whether there is slow or rapid coagulation. This is shown graphically in Figure 5 and by the data given in Table 11.



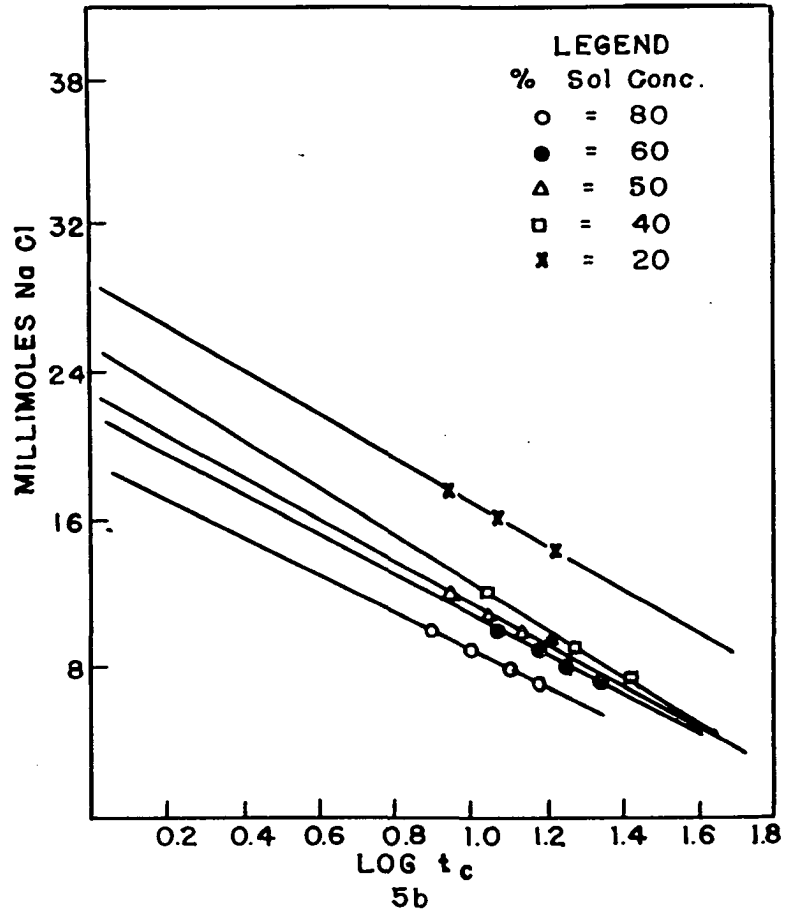


Fig. 5 Critical time as a function of the concentration of NaCl for Sol A_5 (P= 510) at several concentrations.

Table 11

Critical time as a function of the concentration of NaCl for Sol $\underline{A}_5$ ($\underline{P}$ = 510) at several concentrations

% Conc. of sol	Conc. of NaCl millimoles/l.	t_c min.	log t_c	m	b
20	8.0	limiting value			
	12.0	30	1.48		
	*14.4	17	1.23		
	16.0	12	1.08		
	17.6	9	0.95	-12.0	29.0
40	4.5	limiting value			
	6.0	44	1.64		
	*7.2	26	1.42		
	9.0	19	1.28		
	12.0	11	1.04	-12.9	25.5
50	4	limiting value			
	6	40	1.60		
	*9	16	1.20		
	10	13	1.11		
	11	11	1.04		
	12	9	0.95	-11.6	23.0
60	4.0	limiting value			
	6.0	32	1.51		
	*7.2	22	1.34		
	8.0	18	1.25		
	8.8	15	1.18		
	10.0	12	1.08	-11.2	22.0
80	3.0	limiting value			
	5.0	33	1.52		
	*7.2	15	1.18		
	8.0	13	1.11		
	9.0	10	1.00		
	10.0	8	0.90	-10.4	19.4

Table 12 gives the data for the coagulation of Sol $\underline{A}_5$ in varying degrees of purity. As in previous tables, the asterisk indicates the beginning of the data on rapid coagulation. As the purity of the sol increases, not only does the concentration of sodium chloride necessary for coagulation become less, but the slope of the exponential function becomes greater. This is an indication of the greater instability of the purified colloid.

According to the Burton Bishop rule, the coagulation value of the univalent ions increases with a decrease in the concentration of the colloid for any given sol. An examination of the intercept values shows that the Burton-Bishop rule holds for all but two of the samples of Sol $\underline{A}_5$. In these two cases where the purities are 119 and 151, there is a scrambling of the order of the coagulation values compared to the concentration of the colloid, but the tendency is toward a reversal of the Burton-Bishop rule. This is particularly true in the case of Sol $\underline{A}_5$ ($\underline{P}$ = 119). Examination of the limiting values as an indication of the order of the slow coagulation values shows that the Burton-Bishop rule is not obeyed until the purity of the sol is about 500. In other words, in rapid coagulation, the Burton-Bishop rule is followed in all cases except in the range of purity of approximately 50 to 150; but in slow coagulation the Burton-Bishop rule is apparent only at very high purity.

Table 12

Coagulation value of NaCl as a function of the purity and concentration of Sol $\underline{A}_5$

Sol P	Sol % Conc.	Conc. of NaCl millimoles/l.	t_c min.	log t_c	m	b
14.7	20	240	limiting value			
		272	45	1.65		
		*320	19	1.28		
		400	14	1.15		
		480	11	1.04	-731	1240
	40	240	limiting value			
		276	39	1.59		
		*300	20	1.30		
		360	15	1.18		
		420	12	1.08		
		480	9	0.95	-500	955
	50	250	limiting value			
		280	32	1.51		
		*300	19	1.28		
		350	13	1.11		
		400	10	1.00		
		450	7	0.84	-360	760
	60	250	limiting value			
		270	32	1.51		
		*280	20	1.30		
		320	15	1.18		
		360	11	1.04		
		400	8	0.90	-348	730
	80	250	limiting value			
		260	55	1.74		
		*280	20	1.30		
		300	14	1.15		
		320	10	1.00		
		360	5	0.70	-130	450
47.0	20	150	limiting value			
		240	30	1.48		
		*272	22	1.32		
		304	15	1.18		
		320	13	1.11		
		400	6	0.77	-24.5	590

(continued)

Table 12 (continued)

Sol P	Sol % Conc.	Conc. of NaCl millimoles/l.	t_c min.	log t_c	m	b
47.0 (cont.)	40	170	limiting value			
		240	35	1.54		
		*288	17	1.23		
		300	15	1.18		
		336	10	1.00		
		360	8	0.90	-21.2	550
	50	190	limiting value			
		200	40	1.85		
		*260	20	1.30		
		280	15	1.18		
		300	12	1.08		
		320	9	0.95	-16.2	475
	60	210	limiting value			
		240	34	1.53		
		*254	24	1.38		
		280	15	1.18		
		300	10	1.00		
		320	7	0.84	-125	425
	80	230	limiting value			
		240	50	1.70		
		*260	23	1.36		
		280	19	1.15		
		300	8	0.90	-88.0	380
119	20	65.0	limiting value			
		70.0	65	1.81		
		*76.8	33	1.52		
		78.4	26	1.41		
		85.0	11	1.04	-19.0	101
	40	60	limiting value			
		70	60	1.78		
		*92	21	1.32		
		102	14	1.15		
		108	10	1.00		
		116	8	0.90	-48.5	165

(continued)

Table 12 (continued)

Sol P	Sol % Conc.	Conc. of NaCl millimoles/l.	t_c min.	log t_c	m	b
119 (cont.)	50	70	limiting value			
		75	80	1.90		
		*85	25	1.40		
		90	14	1.15		
		95	9	0.95		
		100	5	0.70	-21.5	115
	60	60	limiting value			
		77	28	1.45		
		*92	13	1.11		
		96	11	1.04		
		112	7	0.84	-81.0	184
	80	70	limiting value			
		78	51	1.71		
		*84	30	1.48		
		96	16	1.20		
		100	14	1.15		
		120	5	0.70	-43.5	150
151	20	24.0	limiting value			
		38.0	50	1.70		
		*40.0	23	1.36		
		43.2	13	1.11		
		44.8	10	1.00	-12.2	56.8
	40	30.0	limiting value			
		35.0	80	1.90		
		*38.4	30	1.48		
		40.8	18	1.25		
		42.0	13	1.11		
		45.0	7	0.84	-10.5	53.8
	60	26.0	limiting value			
		34.0	63	1.80		
		*36.0	36	1.56		
		38.4	27	1.42		
		40.0	21	1.32		
		42.0	15	1.18	-15.5	60.5

(continued)

Table 12 (continued)

Sol P	Sol % Conc.	Conc. of NaCl millimoles/l.	t_c min.	log t_c	m	b
151 (cont.)	80	28	limiting value			
		35	63	1.80		
		*40	16	1.20		
		42	10	1.00		
		44	8	0.90	-11.5	54.2
262	20	14.0	limiting value			
		18.0	40	1.60		
		*20.0	21	1.32		
		22.4	18	1.25		
		24.0	15	1.18	-28.8	58.0
	40	12.0	limiting value			
		16.0	45	1.65		
		*18.0	22	1.34		
		21.6	14	1.15		
		24.0	11	1.04	-19.7	44.5
	60	12.0	limiting value			
		14.0	50	1.70		
		*16.0	26	1.41		
		18.0	17	1.23		
		20.0	12	1.08		
		21.6	9	0.95	-12.7	33.7
	80	10.0	limiting value			
		14.0	55	1.74		
		*16.0	34	1.53		
		16.8	21	1.32		
		18.0	14	1.15		
		20.0	8	0.90	-7.2	26.5

(continued)

Table 12 (continued)

Sol P	Sol % Conc.	Conc. of NaCl millimoles/l.	t_c min.	log t_c	m	b
510	20	8.0	limiting value			
		12.0	30	1.48		
		*14.4	17	1.23		
		16.0	12	1.08		
		17.6	9	0.95	-12.0	29.0
	40	4.5	limiting value			
		6.0	44	1.64		
		*7.2	26	1.42		
		9.0	19	1.28		
		12.0	11	1.04	-12.9	25.5
	50	4.5	limiting value			
		6.0	40	1.60		
		*9.0	16	1.20		
		10.0	13	1.11		
		11.0	11	1.04		
		12.0	9	0.95	-11.6	23.0
	60	4.0	limiting value			
		6.0	32	1.51		
		*7.2	22	1.34		
		8.0	18	1.25		
		8.8	15	1.18		
		10.0	12	1.08	-11.2	22.0
	80	3.0	limiting value			
		5.0	33	1.52		
		*7.2	15	1.18		
		8.0	13	1.11		
		9.0	10	1.00		
		10.0	8	0.90	-10.4	19.4

In most of the work published on the Burton-Bishop rule, the studies were made in such a way as to involve only slow coagulation; i.e., the times involved in the measurements were over an hour in length. Thus previous work indicated that if the colloid were sufficiently pure, hydrous ferric oxide would show the Burton-Bishop relationship, which is in agreement with the work here reported. The only previous investigations which appeared to give results in the rapid coagulation range were made by Kaufmann (1940), using Wannow's (1937) method for determining coagulation values. This procedure, previously described and discussed in this thesis, does not seem to be adequate as an absolute method, but it does appear to give values which fall in the upper zone of rapid coagulation. However, the work of Kaufmann was done entirely on the very highly purified hydrous ferric oxide, Sorum sol, and therefore his results would be expected to show the Burton-Bishop relation even though some of his values fell just within the slow coagulation range.

No investigation was made of the changes taking place in the hydrous ferric oxide sol of medium purity as evidenced by the scrambling of coagulation values. However, this characteristic was observed in all series in which the predominating ion was univalent. For example, Table 13, giving the data for the coagulation of Sol A_6 with potassium chloride, shows the scrambling effect as well as the relationship of slow and rapid coagulation values and the Burton-Bishop rule.

Table 13

Coagulation values of KCl as a function of the purity and concentration of Sol $\underline{A}_6$

Sol P	Sol % Conc.	Conc. of KCl millimoles/l.	t_c min.	log t_c	m	b
26.5	20	120	limiting value			
		*320	25	1.40		
		368	23	1.36		
		384	21	1.32	-999	1700
	40	160	limiting value			
		*360	16	1.20		
		420	11	1.04		
		450	10	1.00		
		480	8	0.90	-400	840
	60	160	limiting value			
		*300	28	1.30		
		320	17	1.23		
		360	12	1.08		
		400	9	0.95	-294	680
	80	200	limiting value			
		*300	18	1.25		
		320	14	1.15		
		340	11	1.04		
		360	9	0.95	-204	555
57.2	20	180	limiting value			
		*288	24	1.38		
		304	18	1.25		
		320	12	1.08		
		336	8	0.90	-110	440
	40	240	limiting value			
		*276	20	1.30		
		288	14	1.15		
		294	9	0.95		
		300	7	0.84	-53.8	345
	50	200	limiting value			
		*275	25	1.40		
		280	21	1.32		
		290	13	1.11		
		300	8	0.95	-58.0	355

(continued)

Table 13 (continued)

Sol P	Sol % Conc.	Conc. of KCl millimoles/l.	t_c min.	log t_c	m	b
57.2 (cont.)	60	200	limiting value			
		*272	34	1.53		
		276	28	1.45		
		280	19	1.28		
		288	11	1.04	-34.8	325
	80	200	limiting value			
		*280	23	1.36		
		290	17	1.23		
		300	14	1.15		
		310	11	1.04	-106.0	420
104	20	80	limiting value			
		*112	42	1.62		
		116	20	1.30		
		120	8	0.90	-17.0	138
	40	50.0	limiting value			
		**51.0	44	1.64		
		51.0	8	0.90		
		51.6	6	0.78	-3.1	56
	50	100	limiting value			
		*140	21	1.32		
		145	11	1.04		
		150	6	0.78	-19.2	165
	60	120	limiting value			
		*140	40	1.60		
		152	18	1.25		
		160	11	1.04	-38.5	200
	80	98	limiting value			
		*116	27	1.43		
		120	8	0.90	-15.0	135
147	20	30	limiting value			
		*40	24	1.38		
		44	17	1.23		
		48	12	1.08		
		56	7	0.84	-29.5	81

(continued)

Table 13 (continued)

Sol P	Sol % Conc.	Conc. of KCl millimoles/l.	t_c min.	log t_c	m	b
147 (cont.)	40	30	limiting value			
		*42	22	1.34		
		48	14	1.15		
		54	9	0.95		
		60	5	0.70	-27.0	79
	60	30	limiting value			
		*40	35	1.54		
		48	16	1.20		
		52	11	1.04		
		56	8	0.90	-24.0	77
	80	30	limiting value			
		*40	46	1.66		
		48	18	1.25		
		50	15	1.18		
		56	8	0.90	-21.2	75
305	20	6.0	limiting value			
		*8.0	25	1.40		
		8.4	20	1.30		
		9.0	14	1.15		
		9.6	9	0.95	-3.55	13
	40	5.0	limiting value			
		*7.2	24	1.38		
		7.8	17	1.23		
		8.1	14	1.15		
		8.4	10	1.00	-3.45	12
	60	4.2	limiting value			
		*6.4	20	1.30		
		6.8	16	1.20		
		7.2	13	1.11		
		8.0	8	0.90	-3.50	11
	80	3.8	limiting value			
		*6.0	23	1.36		
		6.4	18	1.25		
		7.0	12	1.08		
		7.8	7	0.84	-2.90	10

This relationship of slow and rapid coagulation and the intersection of the exponential function for several concentrations were characteristic of all coagulation studies made with sodium and potassium chloride. As with Sol $\underline{A}_5$ coagulated by sodium chloride, examination of the values of $\underline{b}$ shows that the Burton-Bishop rule holds for all degrees of purity except for the middle range between 50 and 150. Likewise, in slow coagulation none of the coagulation values were in the order indicating the Burton-Bishop relation until the sol was of relatively high purity, in the neighborhood of 305.

Table 14 shows the relationship, for four sols, between purity of the sol and agreement with the Burton-Bishop rule for both rapid and slow coagulation by sodium and potassium chloride. The absence of agreement with the Burton-Bishop relation in the case of rapid coagulation always coincided with the scrambling effect. In general, the scrambling effect always takes place in the range of purities of approximately 50 and 150. The Burton-Bishop effect always appears in slow coagulation if the sol has a purity of 250 or higher.

Sodium chloride was also used in coagulating the colloids prepared by the other two methods, i.e., the $\underline{B}$ and $\underline{C}$ sols. As previously noted, some difficulty was encountered in determining the critical time for these colloids. It was impossible to determine the critical time for high concentrations of either the $\underline{B}$ or $\underline{C}$ sol, and impossible to determine

Table 14

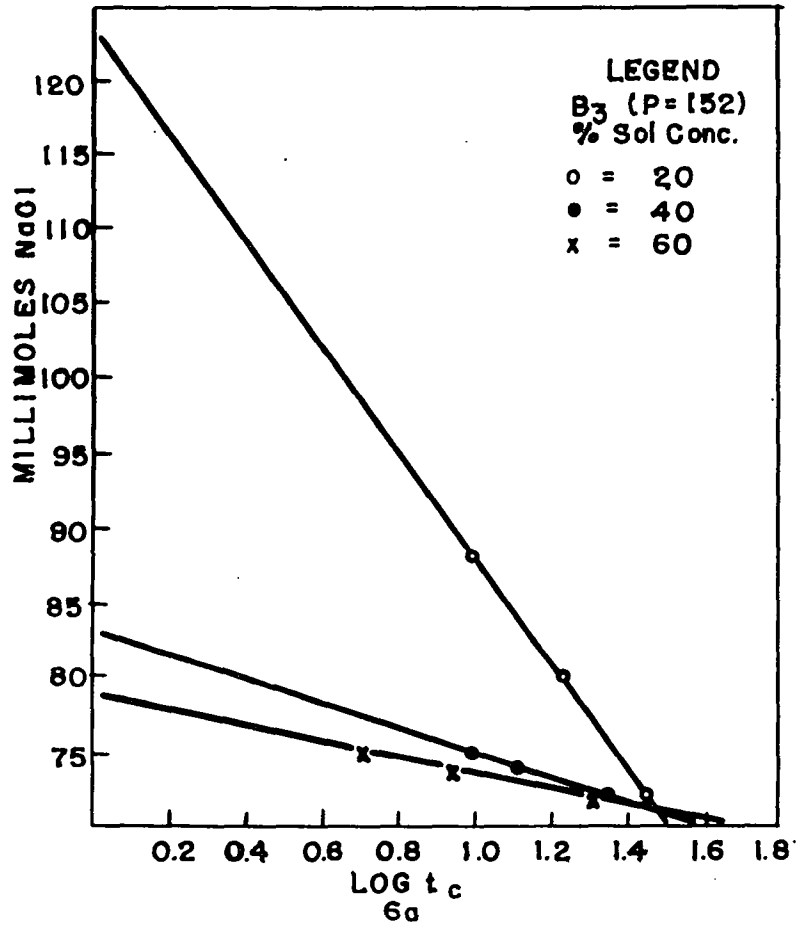
Relationship of Burton-Bishop rule to rapid and slow coagulation and to the purity of several sols
(Plus and minus signs indicate agreement and disagreement with the rule.)

Sol No.	Sol P	Electrolyte	Agreement with Burton-Bishop rule: rapid coagulation	Agreement with Burton-Bishop rule: slow coagulation
A_5	14.7	NaCl	+	-
	47.0		+	-
	119.0		-	-
	151.0		-	-
	262.0		+	+
	510.0		+	+
A_3	21.3	NaCl	+	-
	47.4		+	-
	67.0		-	-
	147.0		+	-
	194.0		+	-
	253.0		+	+
A_3	21.3	KCl	+	-
	47.4		+	-
	147.0		-	-
	194.0		+	-
	253.0		+	+
A_6	26.5	KCl	+	-
	57.2		-	-
	104.0		-	-
	147.0		+	-
	305.0		+	+

the critical times on any of the C sol after it had been dialyzed more than 14 hours, i.e., had a purity greater than 32. From the available data, however, it may be shown that the tendencies for intersecting lines at average purities held with these preparations as well as with the A colloid. Table 15 gives the data and Figure 6 the graphical representation showing the exponential function of the critical time. Further investigation would have to be made in order to give any definite statement on the similarities or differences of the A, B, and C sols and the Burton-Bishop relationship.

It was found that over a period of a week to ten days, aging had no effect on the determination of coagulation or critical time. However, additional aging caused an increase in instability of the sol, which was indicated by two facts: the decrease in the concentration of electrolyte needed to produce coagulation and the increase in the slope of the exponential function. Table 16 gives data showing typical changes in the concentration of electrolyte and the slope for a given concentration of a given sol. In no case did aging change the order of the coagulation values for various concentrations of a given sol; the changes for Sols B and C were similar to those obtained with A.

The Burton-Bishop rule states that the coagulation value of a divalent electrolyte is independent of the concentration of the sol, and that the coagulation value of a trivalent electrolyte varies directly with the concentration of the sol.



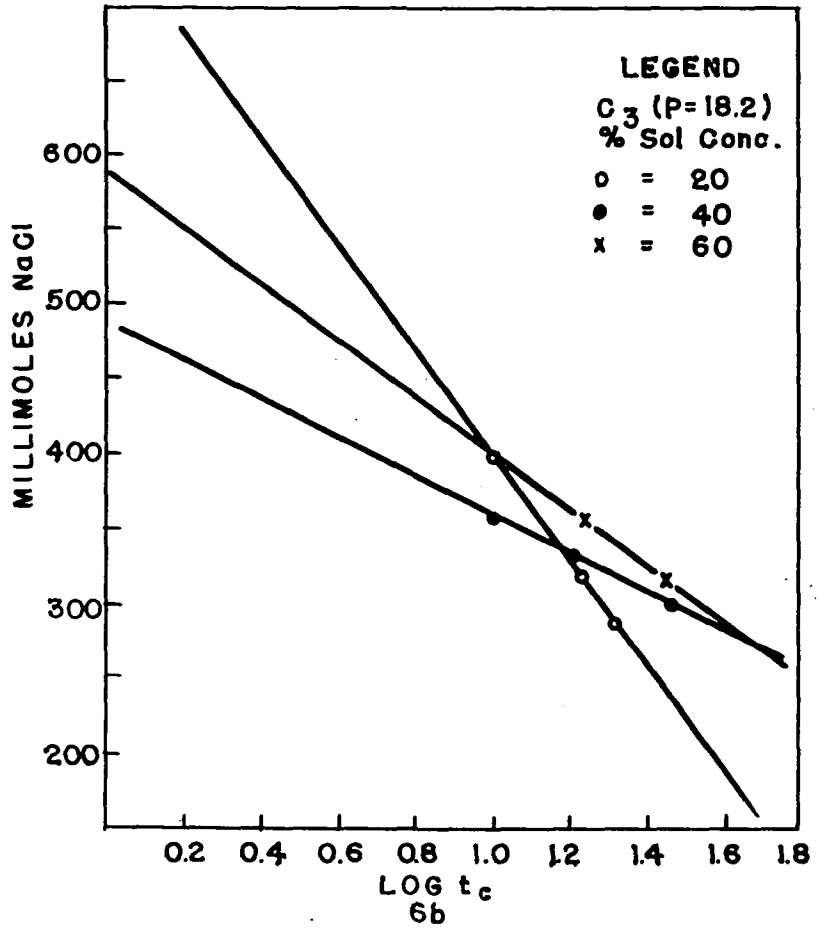


Fig. 6 Critical time as a function of the concentration of NaCl for Sol B_3 and Sol C_3 at several concentrations

Table 15

Critical time as a function of Sol B_3 and Sol C_3 at several concentrations

Sol P	Sol % Conc.	Conc. of NaCl millimoles/l.	t_c min.	log t_c	m	b
	B_3					
152	20	72	28	1.45		
		80	17	1.23		
		88	10	1.00	-35	123
	40	72.0	23	1.36		
		73.8	13	1.11		
		75.0	10	1.00	-8.1	83
	60	72.0	21	1.32		
		73.6	9	0.95		
		80.0	5	0.70	-4.6	78
	C_3					
18.2	20	288	21	1.32		
		320	17	1.23		
		400	10	1.00	-350	750
	40	300	30	1.47		
		336	16	1.23		
		360	10	1.00	-127	487
	60	320	28	1.45		
		360	17	1.23		
		400	10	1.00	-190	590

Table 16

Coagulation values of NaCl as a function of the aging of several sols

Sol			Freshly prepared					Aged 3 months				
No.	P	% conc.	NaCl conc. m.moles/l.	t_c min.	log t_c	m	b	NaCl conc. m.moles/l.	t_c min.	log t_c	m	b
A_3	21.3	50	375	18	1.25			250	19	1.28		
			400	15	1.18			275	14	1.15		
			450	11	1.04			300	10	1.00	-180	480
			500	8	0.90	-340	802					
A_3	67.0	50	110	25	1.40			90	19	1.28		
			120	17	1.23			95	14	1.15		
			130	12	1.08			100	11	1.04	-48	150
			150	6.5	0.81	-69	205					
A_3	253	50	23.0	17	1.23			22.5	30	1.48		
			25.0	13	1.11			23.5	18	1.25		
			27.0	10	1.00			25.0	8	0.90	-4.4	29
			30.0	7	0.84	-18	45					
B_3	152	40	72.0	23	1.36			66.0	17	1.23		
			73.8	13	1.11			66.5	14	1.15		
			75.0	10	1.00	-8.1	83	67.0	8	0.90	-3.3	70
B_3	∞	40	7.0	34	1.53			5.4	23	1.36		
			7.8	12	1.08			6.0	16	1.20		
			9.0	6	0.78	-4.1	12.2	7.0	8	0.90	-3.5	10
C_3	21.7	40	98	19	1.28			90	21	1.32		
			110	16	1.20			100	18	1.25		
			120	14	1.15	-183	330	120	12	1.08	-120	250

Therefore an investigation was made of the correlation of rapid coagulation effects and the Burton-Bishop rule, using potassium sulfate and potassium ferricyanide. Lower concentrations, 5 to 40 per cent, of the sol were used because it was impossible to obtain sufficient critical times to determine a straight line with concentrations of a sol higher than 40 per cent. This action of the higher concentrations of sols was peculiar to coagulation with both potassium sulfate and potassium ferricyanide. With these electrolytes, coagulation was so rapid as to give a critical time of 1 to 3 minutes, or was so slow as to give no coagulation in 1 to 2 hours.

Data for the coagulation of Sol $\underline{A}_7$ at several purities by potassium sulfate are presented in Table 17. The slopes of exponential functions determined for various concentrations of a given purity of sol show that the lines tend to be parallel. This indicates that the order of coagulation values for both slow and rapid coagulation will be the same. The coagulation values of potassium sulfate were found to decrease slightly and then increase as the concentration of the sol increased. This slight minimum occurred at 10 or 20 per cent concentration of the sol. That is, the order of the intercept values indicated that potassium sulfate had a tendency to act like an electrolyte with a univalent dominating ion when coagulating low concentrations of the sol.

Table 17

Coagulation values of K_2SO_4 as a function of the purity and concentration of Sol $\underline{A}_7$

Sol P	Sol % Conc.	Conc. of K_2SO_4 millimoles/l.	t_c min.	log t_c	m	b
28.9	5	0.171	31	1.49		
		0.190	16	1.20		
		0.208	8	0.90	-0.058	0.260
	10	0.180	20	1.30		
		0.189	14	1.15		
		0.197	11	1.04	-0.057	0.255
	20	0.176	19	1.28		
		0.184	14	1.15		
		0.192	10	1.00		
		0.208	5	0.70	-0.053	0.245
	30	0.168	32	1.50		
		0.181	19	1.28		
		0.183	18	1.25		
		0.189	14	1.15	-0.058	0.255
	40	0.312	14	1.15		
		0.318	12	1.08		
		0.324	10	1.00		
		0.360	3	0.40	-0.07	0.395
60.3	5	0.190	32	1.50		
		0.199	20	1.30		
		0.204	14	1.15		
		0.219	7	0.84	-0.040	0.250
	10	0.180	23	1.36		
		0.186	14	1.15		
		0.189	12	1.08		
		0.197	7	0.84	-0.033	0.225
	20	0.206	20	1.30		
		0.211	16	1.20		
		0.216	12	1.08		
		0.240	3	0.48	-0.041	0.260

(continued)

Table 17 (continued)

Sol P	% Conc.	Conc. of K_2SO_4 millimoles/l.	t_c min.	log t_c	m	b
60.3 (cont.)	30	0.245	30	1.48		
		0.252	18	1.25		
		0.260	11	1.04		
		0.266	8	0.90	-0.038	0.300
	40	0.300	29	1.45		
		0.306	20	1.30		
		0.310	12	1.08		
		0.324	3	0.48	-0.023	0.335
114	5	0.190	38	1.58		
		0.208	16	1.20		
		0.214	12	1.08		
		0.219	10	1.00	-0.045	0.262
	10	0.173	17	1.23		
		0.180	13	1.11		
		0.189	8	0.90		
		0.198	5	0.70	-0.048	0.232
	20	0.168	17	1.23		
		0.175	12	1.08		
		0.185	7	0.84		
		0.192	5	0.70	-0.047	0.225
	30	0.210	25	1.40		
		0.224	12	1.08		
		0.238	5	0.70	-0.040	0.267
201	5	0.190	23	1.36		
		0.192	21	1.32		
		0.199	12	1.08		
		0.219	7	0.84	-0.035	0.237
	10	0.180	19	1.28		
		0.185	15	1.18		
		0.193	9	0.95	-0.034	0.225
	20	0.168	25	1.40		
		0.175	15	1.18		
		0.180	10	1.00		
		0.185	7	0.84	-0.028	0.208

(continued)

Table 17 (continued)

Sol P	Sol % Conc.	Conc. of K_2SO_4 millimoles/l.	t_c min.	log t_c	m	b
201 (cont.)	40	0.180	30	1.48		
		0.182	21	1.32		
		0.186	18	1.25		
		0.192	12	1.08	-0.035	0.230
300	5	0.146	28	1.45		
		0.150	21	1.32		
		0.152	17	1.23	-0.041	0.205
	10	0.144	31	1.49		
		0.148	22	1.34		
		0.151	18	1.25		
		0.153	16	1.20	-0.041	0.202
	20	0.120	25	1.40		
		0.128	16	1.20		
		0.131	13	1.11		
		0.136	11	1.04	-0.043	0.180
	30	0.140	38	1.58		
		0.147	25	1.40		
		0.153	16	1.20	-0.041	0.205
	40	0.144	30	1.48		
		0.149	20	1.30		
		0.153	17	1.23		
		0.157	12	1.08	-0.041	0.205

On the other hand, at higher concentrations the electrolyte had a tendency to behave as though the dominating ion were trivalent. These tendencies were shown throughout the complete range of sol purities used but were at a minimum with highly purified sols. In conformity with the Burton-Bishop rule, the coagulation values of potassium sulfate show an intermediate position between the monovalent and trivalent ions.

Investigation of potassium ferricyanide as the added electrolyte was hampered by two factors: inability to use high concentrations of the colloid due to the quick change from rapid to slow coagulation, and the gelation caused by agglomeration of the sol. Both of these changes have been discussed in previous sections of this thesis. Sufficient data were obtained, and are listed in Table 18, to show that the exponential function of critical time against the concentration of the electrolyte gives a series of parallel lines for different concentrations of the same sample of sol. As with potassium sulfate, this indicates that the coagulation values of potassium ferricyanide will be in the same order for different sol concentrations in both rapid and slow coagulation. The data also show that the coagulation values of the electrolyte vary directly with the concentration of the colloid, which is in agreement with the Burton-Bishop rule.

Table 18

Coagulation values of $K_3Fe(CN)_6$ as a function of the purity and concentration of Sol $\underline{A}_5$

Sol P	Sol % Conc.	$K_3Fe(CN)_6$ conc. millimoles/l.	t_c min.	log t_c	m	b
26.9	5	0.0219	25	1.40		
		0.0225	19	1.28		
		0.0228	15	1.18	-0.0034	0.0268
	10	0.0387	30	1.48		
		0.0396	15	1.18		
		0.0405	10	1.00	-0.0043	0.0448
	15	0.0555	16	1.20		
		0.0560	12	1.08		
		0.0565	9	0.95	-0.0040	0.0603
	20	0.0662	10	1.00		
		0.0669	6	0.78		
		0.0677	4.5	0.65	-0.0042	0.0704
52.2	5	0.0214	20	1.30		
		0.0220	14	1.15		
		0.0228	8	0.90	-0.0033	0.0258
	10	0.0335	28	1.45		
		0.0342	15	1.18		
		0.0349	10	1.00	-0.0031	0.0380
	15	0.0454	36	1.56		
		0.0460	14	1.15		
		0.0464	10	1.00	-0.0035	0.0500
	20	0.0595	35	1.54		
		0.0608	16	1.20		
		0.0614	11	1.04	-0.0038	0.0653

It has been found that critical times may be used in determining the relationship of the sol concentration to the coagulation values of an electrolyte. The order of the intercepts of the exponential function of the critical time against the concentration of the electrolyte indicates the order of the rapid coagulation values. If the straight lines are approximately parallel, the order of coagulation values in both rapid and slow coagulation are the same. However, if the lines intersect, the coagulation values in slow coagulation may be, but are not necessarily, in the inverse order to those of rapid coagulation. If the dominating ion is univalent, the order of the rapid coagulation values is in accord with the Burton-Bishop rule with all purities of the hydrous ferric oxide sol except between approximately 50 and 150. However, the order of slow coagulation values for univalent electrolytes agrees with the Burton-Bishop relation only if the purity is 250 or higher. If the dominating ion is divalent, the behavior of the electrolyte is intermediate between the monovalent and trivalent ions, in accord with the Burton-Bishop rule. Although, for reasons previously noted, complete investigation could not be made of coagulation with a dominating trivalent ion, the data show that rapid coagulation values vary with the sol concentration, as has been expressed in the Burton-Bishop relation.

Further investigation should be made of the shifting

minimum found when potassium sulfate was the added electrolyte. The cause of the scrambling of the coagulation values in some sols when the dominating ion was univalent should also be studied.

SUMMARY AND CONCLUSIONS

1. Hydrous ferric oxide sols were prepared by three methods involving the hydrolysis of ferric chloride. The properties of the sols were compared both when freshly prepared and when aged for about three months. The two sols prepared by hydrolysis under reflux conditions were similar in their properties but were somewhat different from the Sorum sol. The purities of the sols were determined as the ratio of the equivalents of iron to the equivalents of chloride. Most of the work discussed in this thesis is based on the Sorum sol, prepared by dropping ferric chloride into boiling distilled water.

2. In coagulation studies a distinction should be made between agglomeration and coagulation. Agglomeration is defined as the collision and adhesion of particles and coagulation as the point of complete agglomeration that will ultimately produce sedimentation. Agglomeration, in terms of the change of light transmission, was followed by means of a KWSZ Photometer. The time at which the direction of the change of light transmission reversed was the time of coagulation, denoted as the critical time (t_c). At the critical time, flocs were visible but no sedimentation was noted until after a time interval of 15 seconds to 1 hour had elapsed.

3. The critical time, within limits, is an exponential function of the concentration of electrolyte. The straight-line relation is found only for relatively small values of the critical time and is indicative of rapid coagulation. The time range involved in the exponential function was from 2 to 45 minutes. Critical times greater than about 45 minutes were indicative of slow coagulation.

4. In the coagulation of hydrous ferric oxide sols with electrolytes containing a dominating univalent ion, the exponential functions of the critical time for different sol concentrations intersect except in cases of highly purified sols when the straight lines tend to be parallel. The intercepts of the exponential functions with the y-axis are indicative of the order of the coagulation values for different sol concentrations up to the point of intersection of the lines. If the intersection occurs within the zone of rapid coagulation, then the order of the slow coagulation values will be the inverse of those for the very rapid coagulation. If the intersection of the straight lines occurs at the end of the zone of rapid coagulation, the order of the slow coagulation values may be, but are not necessarily, the inverse of the rapid. With electrolytes containing dominant univalent ions, the order of the rapid coagulation values as indicated by the intercepts always increased with a decrease of the sol concentration except for a scrambling effect at

purities of about 50 to 150. This relation is in good accord with the Burton-Bishop rule. However, the order of slow coagulation values was in agreement with the Burton-Bishop relation only when the sol purity was 250 or higher. The electrolytes used were potassium and sodium chloride.

5. The exponential functions for different sol concentrations when potassium sulfate was employed were parallel, indicating that the order of rapid and slow coagulation values was the same. An examination of the intercept values shows that there is a slight decrease of the coagulation values for low sol concentration and a slight increase at higher concentrations. That is, the potassium sulfate has a slight tendency to behave as an electrolyte with a dominant univalent ion for low sol concentrations and as though it were trivalent for higher concentrations. The coagulation values thus indicated an intermediate position between the behavior of univalent and trivalent ions and a tendency toward being independent of the sol concentration. This is in accord with the Burton-Bishop rule for divalent ions.

6. Since potassium ferricyanide caused gelation as well as coagulation of the sol, a complete series of sols of different purities could not be investigated. Sufficient data were obtained, however, to show that the exponential functions of critical time and concentration of electrolyte were parallel for different sol concentrations. The order

of the intercept values indicated that the coagulation values of the electrolyte decreased with a decrease in sol concentration, which is in agreement with the Burton-Bishop rule.

7. Further investigation should be made of the reason for the scrambling effect noticed for certain purities of the sol when coagulated by sodium chloride and potassium chloride. Investigation should be made also of the slight tendency of potassium sulfate to show coagulation behavior typical both of univalent and of trivalent ions.

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